ARSENIC IN LEACHATES FROM MINE WASTE ROCKS

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ABSTRACT

This research dealt with the leaching of arsenic containing waste rocks from a proposed gold mine site at Reefton, New Zealand. Then it established the acidity and concentrations of Fe, sulfate, As(V) and As(III) released as a result of leaching experiments which simulated the weathering process. It also determined the arsenic concentrations that were released from old mine workings into the Devils Creek sediments catchment and concentrated into sediments. The Devils Creek catchment is located downstream from the proposed mine.

Acid mine drainage (AMD) results from oxidation of sulfide bearing rocks and deposits (e.g. FeS and FeS_2). It is characterised by elevated concentrations of sulfate and iron and low pH. As(V) and As(III) may also be a component in AMD from the oxidation of FeAsS. Biologically As(III) is considered the more toxic form.

Methods were developed for the measurement of arsenic species (As(V) and As(III)) in leachates derived from mine waste rocks. These were applied to freshwater samples and sediment extracts. These included:

- A field method for the on-site fractionation of arsenic in fresh waters using XAD-4 and Chelex-Fe(III) resins. In this two-step process the XAD-4 resin was used to isolate and pre-concentrate natural organic matter (NOM) and therefore the arsenic fraction associated with it through iron bound to the NOM. In the second step Fe(III) modified Chelex 100 resin was used to selectively preconcentrate As(V) from water samples. Thus the combined method achieved discrimination between free and bound fractions of As(V) and the separation of As(V) from As(III).
- A flow injection analysis protocol based on spectrophotometric detection was modified to increase its sensitivity for measurement of arsenic species in leachates derived from waste rocks. The method was effective for the determination of arsenate. Arsenite was measured by prior oxidation with iodate.

Study on the Devils Creek catchment established the existing baseline levels of arsenic in the fresh water and sediments. The water contains high levels of arsenic. Most of the arsenic in Devils Creek water is soluble. As(V) is the predominant species of which a minor fraction (13-28%) is bound to NOM. It was also established that arsenic was associated with Fe and Al rich phases in the Devils Creek sediments. Due to the high accumulated arsenic load in the sediments, further uptake of arsenic from the water column is no longer viable because potential binding sites in the sediments have been saturated.

Leaching simulation on mine basic waste rocks (GB 13) and an acidic sandstone were conducted using a variety of leachants applicable to the field, then quantifying the Fe, As(III), As(V), heavy metals and acidity in the leachates. It was established that the sandstone rock had the greater potential to produce acid mine drainage (AMD). Its leachates give a high acidity (pH 2.9-3.4) compared to leachates of the GB 13 waste rock which have a weakly basic pH of 7.2. The dominant arsenic species in leachates of both rock types is As(V). The concentrations of arsenic, soluble Fe and heavy metals leached from the sandstone were greater than those leached from GB 13.

The interactions of arsenate with other components of AMD and natural organic matter were examined. It was established that ferrihydrite semi-quantitatively and rapidly removes arsenate from solution. The arsenate adsorption is inhibited by competing ions in the following order: sulfate > FA ≅ HA. Complexes of HA-Fe(III) and FA-Fe(III) bind arsenate as 1:1 complexes through the Fe(III).

Investigations were made on the use of limestone for the control of arsenic in mine waste rock leachates. It was established that where acidic leachate contacts limestone the pH rises as a result of neutralisation reactions. Subsequently there is a precipitation of Fe(III) and retention of As(V) on the $Fe(OH)_3$. As(III) is oxidised by Fe^{3+}(aq) and $Fe(OH)_3$. On contact with the limestone surface, As(III) is also retained and oxidised. Fe(III) impurities in the limestone are responsible for the uptake of both As(V) and As(III). Insoluble calcium arsenates or arsenites are not formed.

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CHAPTER 1

INTRODUCTION

1.1 ARSENIC IN THE ENVIRONMENT

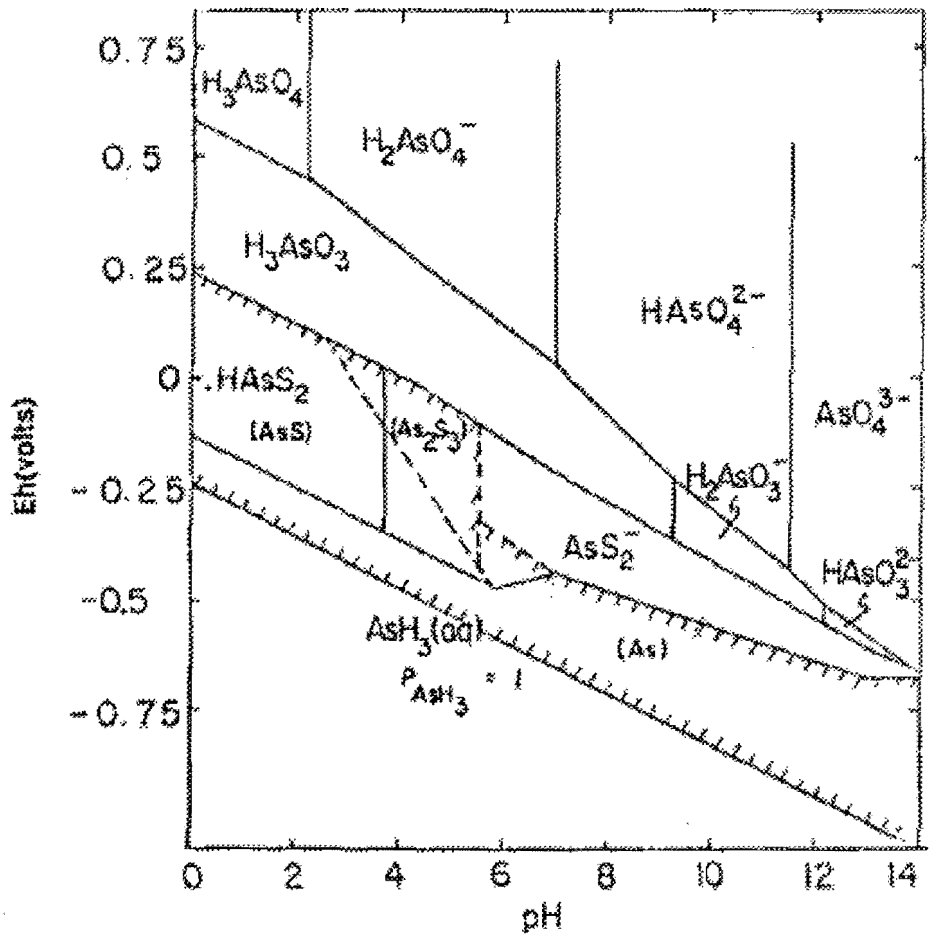
1.1.1 Arsenic speciation in aqueous systems

Arsenic is a member of group 15 of the periodic table; this group contains nitrogen, phosphorus, antimony, and bismuth. The physical appearance of the element resembles that of a metal, so it is referred as a metalloid to distinguish it from a true non-metal.

This thesis deals with arsenic derived from leachates of mine waste rocks. Only inorganic arsenic is likely to be significant in these leachates and therefore inorganic arsenic species only have been studied. The concentrations of arsenic found in fresh waters are 10^{-7}-10^{-5} M and in polluted waters typically 10^{-5}-10^{-4} M (Pierce and Moore, 1982; Mok and Wai, 1987, Wai *et al.* 1986). In the mining industry, some mine-polluted water and tailing water from mineral processing plants contains arsenic.

The speciation of inorganic arsenic in fresh waters is a function of pH and E_h. Thermodynamic predictions provide useful insight into its equilibrium chemistry and Figure 1.1 shows the stability of arsenic in water. In oxygenated waters, As(V) is dominant, existing in anionic forms of $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} over the pH range of 5-12. Under mildly reducing (anoxic) conditions, As(III) is the more stable oxidation state, forming the arsenious acid species H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{2-}$.

Figure 1.1 E_h-pH diagram for arsenic at 25 °C and one atmosphere with total arsenic 10^{-5} M and total sulfur 10^{-3} M. Solid species are enclosed in parentheses in the cross-hatched areas; this indicates solubility less than $10^{-5.3}$ M (Ferguson and Gavis, 1972).



The acid-base reactions of inorganic arsenic species (Hering and Wilkie, 1996) are given in Table 1.1

Table 1.1 The acid base reactions of arsenic species and their equilibrium constants

Reaction	Log K
$AsO_4^{3-} + H^+ = HAsO_4^{2-}$	11.6
$AsO_4^{3-} + 2H^+ = H_2AsO_4^-$	18.35
$AsO_4^{3-} + 3H^+ = H_3AsO_4$	20.6
$AsO_3^{3-} + H^+ = HAsO_3^{2-}$	13.41
$AsO_3^{3-} + 2H^+ = H_2AsO_3^-$	25.52
$AsO_3^{3-} + 3H^+ = H_3AsO_3$	34.74

Below pH 5.5, in the presence of sulfides and for an E_h value of approximately 0 Volts, precipitation of AsS (realgar) or As_2S_3 (orpiment) may remove soluble As(III) and exert control over trace arsenic concentrations. $HAsS_2$ is predominant in the presence of sulfide and AsS_2^- predominates at pH greater than 3.7. At lower E_h elemental As is thermodynamically stable. At low E_h values, arsine (AsH_3) may also be formed (Ferguson and Gavis, 1972; Ferguson and Anderson, 1974).

Although thermodynamics provides a basis for predicting possible changes in a system subjected to non-equilibrium conditions, it gives no insight into the rate at which those changes can occur. In general, acid-base reactions can be assumed to occur instantaneously, whereas changes in oxidation state may require indeterminate periods in fresh waters. For instance, the conversion of As(III) to As(V) in oxygenated water is thermodynamically favoured, yet the transformation may take days to months depending on specific conditions. Presence of other cations and complexes can enhance the oxidation (Ferguson and Anderson, 1974).

In fresh waters, arsenic is distributed between the dissolved and particulate phases. This is a critical factor, which affects the mobility, reactivity, bioavailability, and toxicity of arsenic (Hering and Wilkie, 1996). Adsorption to suspended and bottom

sediments can control the arsenic concentrations in fresh waters. Arsenic can also be accumulated by algae, bacteria and higher organisms up the food chain, such as fish (Maeda, 1994).

Sediments may contain arsenic in a variety of mineral forms including FeAsS and As_2S_3. Arsenic levels are often elevated when iron or manganese levels are high in sediments, and the element is enriched in the Fe/Mn phases. This is because iron(III) and manganese(IV) exert a strong influence on the arsenic concentrations in the aqueous environment through adsorption to their very insoluble hydrous oxides (Dzombek and Morel, 1990; Fergusson, 1990). These elements can form arsenopyrite (FeAsS) and $Mn_3(AsO_4)_2$ (Edwards, 1994). It is likely that $FeAsO_4$ also forms by substitution for the phosphate bound to Fe(II) in the sediments. Kaolinite, illite, montmorillonite (Manning and Goldberg, 1996; Manning and Goldberg, 1997), and amorphous aluminium hydroxide (Holm, 1987, Ghosh, 1987) are also responsible for the adsorption of arsenic. Other elements, which control arsenic levels, are calcium and barium. The solids formed are $Ca_3(AsO_4)_2$ and $Ba_3(AsO_4)_2$ (Boyle and Jonasson, 1973; Masscheleyn *et al.* 1991).

Arsenic can be released into the water column from sediments upon reduction of Fe(III) to Fe(II) and release of As(V). And As(III) from As_2S_3 can be released in the presence of HS^-. As(V) is the more strongly adsorbed to sediments. Further interconversion between As(III) and As(V) can occur in sediments, depending on the anoxic/oxic conditions of the sediment environment (Fergusson, 1990). Mn(IV) and Fe(III) oxides in sediments can oxidise As(III) to As(V), hence influencing the arsenic oxidation states in the sediments (Oscarson *et al.* 1980; Oscarson *et al.* 1981; Driehaus *et al.* 1995).

1.1.2 Arsenic toxicity and health effects

Recent epidemiological studies on carcinogenicity of arsenic have triggered increased concern about the concentration of arsenic in drinking water and have prompted reevaluation of arsenic's current maximum contaminant level (MCL) of 50 μg/L. The

range of arsenic MCL proposed by the US Environmental Protection Agency (USEPA) is 2-20 μg/L. In 1993, the World Health Organisation (WHO) decreased the guideline from 50 μg/L to a value of 10 μg/L (Swedlun *et al.* 1996).

Humans are exposed to arsenic primarily from air, food and water. The chemical forms of arsenic have an influence on its toxicity. Biologically, As(III) is considered the most toxic form (Mok and Wai, 1987). Toxicity of arsenic species to humans decreases in the following order: arsenite > arsenate > monomethylarsonic acid > dimethylarsinic acid > arsenobetaine (Sturgeon *et al.* 1989; Reay, 1973). Monomethylarsonic acid, dimethylarsinic acid and arsenobetaine are organoarsenic compounds. The mechanism of toxicity for trivalent arsenic arises from its high affinity for thiol groups, which are present at the active centers of a large number of enzymes (Soto *et al.* 1995). Therefore, trivalent arsenic interferes with enzymes by bonding to HS- and HO- groups, thus inhibiting enzymes such as the pyruvate oxidase system, δ-oxidase, choline oxidase and transaminase. It appears that one of the body's defences against arsenic is alkylation, producing the less toxic alkylarsenic(V) compounds $CH_3AsO(OH)_2$ and $(CH_3)_2AsO(OH)$, which are excreted from the body.

The effects of acute arsenic poisoning through oral intake are cirrhosis of the liver, intense abdominal pain, nausea, vomiting, and diarrhea from damage to the gastrointestinal tract, finally coma and death. Respiratory effects from inhalation are irritation in the nose and throat. In addition, neurological effects occur such as headache, restlessness and irritability. Ingested arsenic affects the skin, and in most severe forms causes cancer. The signs of arsenic toxicity on the skin are hyperpigmentation and hyperkeratosis on the palms of hands and soles of feet. Blackfoot disease is a result of long time exposure through ingestion.

Arsenic can affect the blood system, interfere with porphyrin biosynthesis, and affect the white blood cells. Effects on the reproductive system, such as spontaneous abortion, have been attributed to arsenic. Loss of hearing has also been associated with arsenic poisoning. Similar to other metals, arsenic affects the renal system. The

peripheral nervous system is also influenced by arsenic (Fergusson, 1990; Dunnette and Morton, 1994, Chen and Lin, 1994).

The occurrence of health problems resulting from arsenic contamination of domestic water has been report in Thailand (Williams *et al.* 1996), Taiwan (Chen *et al.* 1985; Chen and Wang, 1990) and Bangladesh (Ahmed *et al.* 1998). The source has been from natural leaching of bedrock containing arsenopyrite. Arsenical skin cancer was diagnosed in the local populations. Measurements showed that arsenic concentrations in the local water supplies exceeded WHO potable water guidelines.

1.2 ENVIRONMENTAL IMPACT OF PYRITE OXIDATION

Economically viable ores (e.g. coal and gold-bearing ores) can contain elevated levels of toxic elements (e.g. heavy metals and As). Mineralised areas of New Zealand contain such ores (Williams, 1974). Through uncontrolled mine waste disposal the toxic elements can be discharged into fresh water streams, through the process of 'acid mine drainage' (AMD).

1.2.1 Acid mine drainage

1.2.1.1 Sources of acid mine drainage

AMD results from the oxidising action of water, air and bacteria on metal sulfides in exposed rocks. Rocks susceptible to oxidation are specifically those containing iron pyrite. These include copper pyrite ($CuFeS_2$), arsenopyrite (FeAsS) and in coal seams, the iron sulphide (FeS_2). The major minerals associated with AMD (Gray, 1996) are given in Table 1.2. AMD may occur naturally, but is promoted by human intervention where sulfidic rock has been exposed as a result of construction, mining and other activities. The potential sources from mining operation include waste rocks, ore stockpiles, tailings waste (Morrell *et al.* 1996), underground mine workings, open mine pits and spent heap leach piles.

AMD occurs when all of the following conditions are met:

i) The waste contains sulfide that reacts chemically and biologically to form acid leachate at a faster rate than it can be neutralised by any alkaline compounds contained in the waste.

ii) The physical properties of the waste are such that they allow both water and oxygen to permeate in sufficient quantities to support chemical and biological reactions.

iii) There is sufficient rainfall to cause water infiltration and/or the waste is located such that surface water passes through it and transports the acid drainage into the environment.

Table 1.2: Major minerals associated with acid mine drainage (Gray, 1996)

Mineral	**Composition**
Arsenopyrite	FeAsS
Bornite	$CuFeS_4$
Chalcocite	Cu_2S
Chalcopyrite	$CuFeS_2$
Covellite	CuS
Galena	PbS
Millerite	NiS
Mobybdenite	MoS_2
Pyrite	FeS_2
Pyrrhotite	$Fe_{11}S_{12}$
Sphalerite	ZnS

AMD is not necessarily confined to mining activities, but can occur naturally whenever sulfide-bearing rock is exposed to air and water. There are naturally occurring springs that are acidic and these are usually located in the vicinity of outcrops of sulfide bearing rock.

1.2.1.2 Consequences of AMD

AMD affects both surface and ground waters in various ways which include chemical, physical, biological and ecological impacts (Gray, 1997). Streams that are affected by AMD are characterised by elevated concentrations of sulfate and iron and a low pH. It also gives rise to elevated concentrations of a variety of metals depending on the host rock geology (Evangelou and Zhang, 1995; Gray, 1996; Allen *et al.* 1996). Studies have shown that typically AMD decreases slowly with time following cessation of mining, as the sulfides are consumed by weathering reactions. In addition, as the water travels down stream, dilution and buffering usually occur, and the pH increases (Rahn *et al.* 1996).

Brooks *et al.* (1982) studied pollution by arsenic in AMD impacted streams and established its effects on aquatic microorganisms The arsenic content of aquatic organisms correlated with the arsenic content in water for mayfly larvae, caddisfly larvae and the banded killifish. In stream sediments (clay and quartz fractions), arsenic levels increased in the vicinity of the mine and remained high in the sediments downstream.

1.2.2 Pyrite oxidation reactions

The oxidation of pyrite is complex because it involves chemical, biological, and electrochemical reactions and it varies with environmental conditions. Factors such as pH, O_2 concentration, specific surface morphology of pyrite, presence or absence of bacteria (most commonly *Thiobacillus ferrooxidans*) and hydrological factors determine the rate of oxidation. There is no single rate law available to describe the overall kinetics of pyrite oxidation for all cases (Evangelou and Zhang, 1995).

Pyrite oxidation is described by the following two sets of reactions:

i) oxidation by oxygen

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1.1)$$

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \quad (1.2)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (1.3)$$

the overall reaction is

$$4FeS_2 + 15O_2 + 14H_2O = 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \quad (1.4)$$

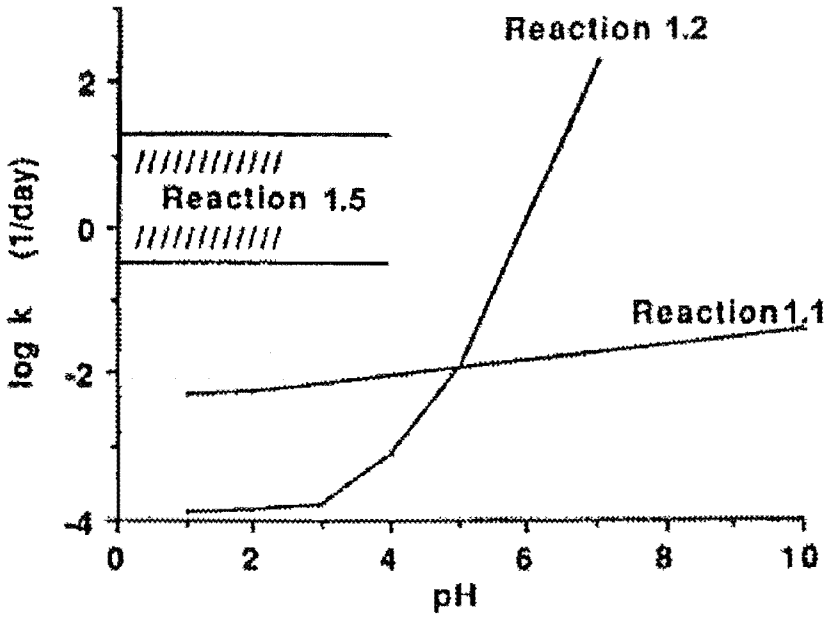
ii) oxidation by Fe^{3+}

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (1.5)$$

The above reactions are mass and charge balanced but do not have any molecular or mechanistic meaning. Pyrite oxidation involves many other metastable species (e.g. thiosulfate). Reaction 1.1 shows the oxidation of pyrite, releasing Fe^{2+} and two protons. In Reaction 1.2 the ferrous ion is oxidised to the ferric ion which hydrolyses to form ferric hydroxide in Reaction 1.3, producing more protons. The sum of Reactions 1.1-1.3 is given by Reaction 1.4.

Upon initiation of the pyrite oxidation, the produced ferric ion oxidises the pyrite as shown in Reaction 1.5. There, pyrite continues to oxidise as long as Fe^{3+} is regenerated. The oxidation of Fe^{2+} to Fe^{3+} is the rate-limiting step (Evangelou, 1995; Gray, 1997), but at pH, less than 3 oxidation is extremely slow (100 days for completion) unless it is catalysed by microorganisms. *T. ferrooxidans* oxidises iron rapidly at pH 2.5-3.5 (Ball *et al.* 1979; Rose and Ghazi, 1997). Also, *T. ferrooxidans* and other sulfur oxidising bacteria such as *T. thiooxidans* can eliminate the need for ferric ion when in the presence of oxygen and an organic substrate (Evangelou, 1995, Evangelou and Zhang, 1995).

Figure 1.2: Comparison of rate constants as a function of pH (Evangelou, 1995) for reaction 1.1 (oxidation of pyrite by O_2), reaction 1.2 (oxidation of Fe^{2+} by O_2) and reaction 1.5 (oxidation of pyrite by Fe^{3+}).



The information relative rates for reactions 1.1-1.5 are illustrated in Figure 1.2. At low pH (<4.5) pyrite is oxidised more rapidly by Fe^{3+} than by O_2, and more rapidly than dissolved Fe^{2+} is oxidised by O_2 to Fe^{3+}. For this reason, Reaction 1.2 is known to be the rate-determining step in abiotic oxidation.

T. ferrooxidans is an acidophilic chemolithotropic organism that resides in geological environments containing pyrite (Evangelou and Zhang, 1995; Evangelou, 1995). In the presence of *T. ferrooxidans* and under low pH conditions pyrite oxidation can be described by Reactions 1.2 and 1.5.

At neutral to alkaline pH, the abiotic rate of Fe^{2+} oxidation increases (Figure 1.2) and the Fe^{3+} concentration decreases rapidly due to formation of the iron (III) hydroxide. Because there is little bacterial mediation at this pH it has been suggested that O_2 is the major oxidant rather than Fe(III). However recent findings (Luther, 1987; Evangelou, 1995; Evangelou and Zhang, 1995) have shown that at circumneutral pH, Fe(III) is the preferred pyrite oxidant and the major role played by O_2 is to oxidise Fe^{2+} thereby

sustaining the sulfide oxidation cycle. Finally, Reaction 1.3 taking place at a pH as low as 3, is a readily reversible reaction that serves as a source as well as a sink for Fe(III) in solution, and is also a major step in the release of acid to the environment.

Overall, the net result of pyrite oxidation is the release of acid, which further contributes to the dissolution of other metals and toxic elements associated with the ore (Mitchell and Walsh, 1975; Stanley, 1986; Bhole, 1994; Yanful *et al.* 1995; Stumm and Morgan, 1970). As the AMD products are transported away from the mine site, the water typically undergoes an increase in pH due to dissolution of basic minerals such as limestone. At values above 3, the Fe^{3+} precipitates as the yellow hydrated Fe^{3+} oxide (Allen *et al.* 1996).

AMD can commence at any time from instantaneously to many decades after the initial disturbance or deposition of the sulfide-containing material. The time lag is a function of the amount of water that passes through the material, the rate at which the sulfide oxidises, the amount of neutralising material available, and neutralisation reaction rates. The rate of reaction also depends on the grain size and morphology of pyrite. Pyrite occurs as acicular forms, coarse-grained masses, euhedral forms, framboidal and polyframboidal forms and octahedral and pyritoheral crystals. It is assumed that framboidal pyrite (which has small particle size, and therefore a large surface area) is the major contributor to the degradation of water quality and the cause of AMD during the process of mining (Evangelou, 1995). If sufficient buffering minerals are present (carbonates or basic aluminosilicates) the pH of the resultant leachate can be basic (Ferguson, 1990).

1.2.3 Review of pyrite oxidation mechanisms

As outlined above, although dissolved O_2 is the initial pyrite oxidant, Fe^{3+} is the major oxidant in the acidic pH region and recent studies have shown that Fe^{3+} can also be an oxidant at circumneutral pH (Moses *et al.* 1987). The rate of pyrite oxidation is faster by Fe^{3+} because Fe^{3+} chemically binds to the pyrite surface while O_2 cannot. Access of O_2 to the surface of the pyrite is restricted to physical adsorption. The difference in

binding between Fe^{3+} and O_2 can be explained based on molecular orbital theory (Luther, 1987; Evangelou and Zhang, 1995).

Luther (1987) proposed a molecular orbital (MO) inner sphere electron transfer process for the pyrite oxidation mechanism, assuming that this electron transfer would proceed via orbitals of the same symmetry. This involves the transfer of electrons from the highest occupied molecular orbital (HOMO) of the reductant (FeS_2) to the lowest unoccupied orbital (LUMO) of the oxidant (e.g. Fe^{3+}). The process requires that all electron transfers would involve the reduced sulfur of the pyrite and the pyrite surface adsorbed oxidant; thus, no electron transfer involves pyrite structural Fe^{2+}. Taking these factors into consideration the HOMO must combine with the LUMO of the same symmetry to ensure proper overlap of the reductant and oxidant orbitals to initiate electron transfer. Therefore, in a linear arrangement of atoms electron transfer will only occur from π^* to π^* orbitals on different species or from σ^* to σ^* but not π^* to σ^*. This Fe^{3+} pyrite oxidation mechanism suggested by Luther (1987) is also consistent with the following experimental observations:

i) sulfoxy species ($S_2O_3^{2-}$) are intermediates produced during pyrite oxidation by either Fe^{3+} or O_2

ii) O_2 does not oxidise $S_2O_3^{2-}$ as readily as does Fe^{3+}. Hence, the sulfoxy species are prevalent in the presence of oxygen.

iii) Water is the source of oxygen for the sulfoxy intermediates and /or sulfate.

The molecular structure of pyrite can be represented as:

$$Fe(II)\text{-}S_A\text{-}S_B \qquad (1.6)$$

Based on the frontier molecular orbital theory described by Luther, the surface exposed S_B in the pyrite structure has unshared pairs of electrons. This produces a slightly negatively charged pyrite surface, therefore attracting molecules or cations willing to share a pair of electrons. Preference is given to those ions or molecules acting as Lewis acids.

Luther (1987) described the oxidation of pyrite by Fe^{3+}. The *first step* involves the removal of a water ligand from $Fe(H_2O)_6^{3+}$ or its hydrolysis product $[Fe(H_2O)_5(OH)]^{2+}$.

$$Fe(H_2O)_6^{3+} = Fe(H_2O)_5^{3+} + H_2O \quad (1.7)$$

The *second step* involves binding of the coordinated $Fe(H_2O)_5^{3+}$ species to the surface of the pyrite through S_B, forming a persulfido bridge.

$$Fe(II)\text{-}S_A\text{-}S_B\text{-}Fe(H_2O)_5^{3+} \quad (1.8)$$

In the *third step*, a symmetrical electron transfer or electron transfer within similar molecular orbitals take place, forming a pyrite surface radical

$$Fe(II)\text{-}S_A\text{-}S_B\text{-}Fe(H_2O)_5^{3+} = Fe(II)\text{-}S_A\text{-}S^{+\bullet}{}_B\text{-}Fe(H_2O)_5^{2+} \quad (1.9)$$

The product of Reaction 1.9 reacts with a further $Fe(H_2O)_6^{3+}$ and with H_2O. It transfers a second electron to $Fe(H_2O)_6^{3+}$ and adds one oxygen atom from H_2O to the pyrite surface. Two H^+ and a coordinated S_2O moiety are produced as follows

$$Fe(II)\text{-}S_A\text{-}S^{+\bullet}{}_B\text{-}Fe(H_2O)_5^{2+} + Fe(H_2O)_6^{3+} + 2H_2O = Fe(II)\text{-}S_A\text{-}S^{\bullet}{}_B\text{-}O + 2Fe(H_2O)_6^{2+} + 2H^+ \quad (1.10)$$

Pyrite electron transfer continues until iron(II) thiosulfate is formed:

$$Fe(II)\text{-}S_A\text{-}S_B(O)_3$$

Detachment from the pyrite surface forms Fe(II) and $S_2O_3^{2-}$ in solution. The overall process is summarised by the equation

$$FeS_2 + 6Fe(H_2O)_6^{3+} + 3H_2O = Fe^{2+} + S_2O_3^{2-} + 6Fe(H_2O)_6^{2+} + 6H^+ \quad (1.11)$$

In the presence of Fe^{3+}, thiosulfate is rapidly oxidised to sulfate

$$5H_2O + S_2O_3^{2-} + 8Fe^{3+} = 8Fe^{2+} + 10H^+ + 2SO_4^{2-} \quad (1.12)$$

The sum of Reactions 1.11 and 1.12 produces Reaction 1.5

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (1.5)$$

Other proposed mechanisms of pyrite oxidation are by dissolved oxygen and by electrochemical pyrite oxidation (Evangelou, 1995; Evangelou and Zhang, 1995). Electrochemical pyrite oxidation is the sum of anodic and cathodic reactions occurring at the surface.

1.2.4 Arsenopyrite oxidation

Arsenic is associated with some gold deposits, usually in the form of arsenopyrite. The arsenic is released from mine waste in the pentavalent state (Brooks *et al.* 1982) and can be leached into fresh water systems. Little information has been reported in the literature on the oxidation of arsenopyrite, but the following reaction has been proposed (Mandl *et al.* 1992):

$$4FeAsS + 13O_2 + 6H_2O = 4H_3AsO_4 + 4FeSO_4 \quad (1.13)$$

The ferrous iron can be oxidised by *T. ferroxidans* to ferric iron ($Fe_2(SO_4)_3$) which in turn can oxidise arsenopyrite by the reaction shown in equation 1.14.

$$FeAsS + Fe^{3+} + 8H_2O = H_3AsO_4 + 2Fe^{2+} + SO_4^{2-} + 13H^+ \quad (1.14)$$

It has also been proposed to proceed via electrochemical mediated reactions, either in solution or on the surface of solids (Perkins *et al.* 1995).

Arsenic(III) can be released through the dissolution of orpiment. The solubility of orpiment (As_2S_3) has been investigated by Webster (1990). The reactions are represented by the following equations:

$$As_2S_3 + 6H_2O = 2H_3AsO_3 + 3HS^- + 3H^+ \quad (1.15)$$

$$3As_2S_3 + 3HS^- + H^+ = 2H_2As_3S_6^- \quad (1.16)$$

Reaction 1.16 is significant as the orpiment reacts to give soluble As(III) sulfides.

1.2.5 Predicting acid mine drainage

There are two main purposes for work on predicting acid generation associated with mine wastes. One is to predict the behavior of individual rock types within the deposit so that a management plan can be developed to control acid drainage and prevent acid toxicity. The second is to predict the overall behavior of the waste rock dump, process waste emplacement, open pit and underground void. It is an extremely difficult and complex task.

Predicting acid generation is the fundamental first step in any mine waste geochemistry assessment and provides the foundation for developing control and management plans. Feasible options for management are determined mainly by the geochemical nature of individual rock types, the quantity of each rock type and the mining schedule.

Prediction techniques are catergorised into three groups:

i) geological assessment.

ii) geological static tests

iii) geological kinetic tests

In geological assessment, comparison is made with other mineral deposits and mine sites. It is a commonly used technique and is based on the assumption that mine sites having the same or similar geological characteristics should have the same potential for acid generation. Geological static tests are simple, rapid and relatively inexpensive tests to qualitatively predict the acid forming potential of a waste rock. Static tests are short-term tests that evaluate the balance between acid generation processes and acid neutralization processes. Methods for static tests include oxidation of sulfide minerals (e.g. reaction with hydrogen peroxide) and dissolution of alkaline carbonates and the weathering of silicates from within the waste rock, as a way of determining the AMD neutralisation potential of the waste rock.

Kinetic tests are commonly used long term-tests and are based on humidity cells, column, batch and sohxlet reactors, field lysimeters, trial dumps, and barrel tests. The major objectives of kinetic tests are:

i) To provide data on the rate of acid generation and acid neutralising reactions under laboratory controlled or on-site conditions.

ii) To provide information on metal release and drainage/seepage quality.

iii) To evaluate various treatment options such as covers, liming, layering inundation and chemical addition (bactericides etc).

Kinetic tests by way of column leaching and batch leaching under laboratory conditions attempt to simulate the weathering processes that lead to acid and base dissolution. In kinetic tests, water is usually added to the rocks or tailings for a period of time and acid producing and consuming reactions are allowed to proceed, and samples of leachates or extracts are collected and analysed. Water application can be either continuous or intermittent, simulating rainfall and alternate exposure to wet and dry conditions. The column test results provide information on the acid-generation characteristics and indicate if the rate of acid generation is significant or negligible over a period of time. They may also be used to study control measures required to alleviate AMD.

A frequent problem with column tests (continuous leaching) is that the sample becomes water saturated and interpretation of results is therefore complicated. If this is

overcome through intermittent application of leachate, column tests could mimic leaching in a waste rock stack. They provide more appropriate data on the geochemical process and leachate chemistry.

1.3 CONTROL PROCESSES FOR ACID MINE DRAINAGE

AMD can be inhibited or its products modified by reaction with other components in the waste or in water infiltrating the waste. Materials that can alleviate acid generation and its products are carbonates and aluminosilicates. AMD can also be inhibited by applying physical, chemical and biological controls.

1.3.1 Metal dissolution and migration in AMD

1.3.1.1 Introduction

A number of physical, chemical, and biological characteristics associated with mine wastes can be used to control arsenic or metal solubility and migration in AMD. The mobilisation of metals is principally controlled by chemical factors. AMD migration is controlled by both chemical and physical factors.

1.3.1.2 Physical control factors

Physical properties and processes influence the AMD migration. These include amount of rainfall, waste permeability, availability of pore water, pore water pressure, and the mechanisms by which the AMD is transported. Humidity and E_h will differ at different depths in the waste and therefore migration occurs at different rates. The solubility of arsenic and metals can be affected by factors such as waste particle size and shape, ambient temperature and pressure of the pore space gases. These properties are secondary to the chemical processes that can cause arsenic and metals to dissolve in AMD.

1.3.1.3 Chemical control factors

The solubility of arsenic (and metals) is controlled by minerals capable of providing buffering reactions such as calcite and dolomite. Aluminosilicates can also make significant contributions to neutralisation of AMD (Banks *et al;* 1997). AMD treatment with limestone has been researched by Skousen *et al* (1997) to investigate the difference in acid neutralisation between armoured and unarmoured limestone. These are limestone which have been coated (armoured) or not coated (unarmoured) with precipitation by ferric hydroxide precipitates. Although armoured limestone is assumed not to react with acid, their results showed that armoured limestone was still 90% as effective in neutralising AMD as the unarmoured limestone. Therefore armoured limestone can still neutralise AMD, but at a reduced rate. Arsenic transport in mine tailings following liming has also been studied by Inskeep *et al.* (1997) and the use of lime for the immobilisation of arsenic has been established.

Other chemical controls include redox potential, adsorption characteristics of the solids and the chemical composition of the AMD. The quality of AMD entering receiving waters is a function of these chemical controls, as they occur at the source of acid generation and along the route of AMD migration. As the AMD moves away from the sulfide source, more acid generating materials may be encountered, causing a further decrease in pH. In some cases, the AMD may be exposed to alkaline material by which partial or complete neutralisation takes place.

Coating surfaces of AMD producing materials with iron phosphate has been investigated as a means of lowering solubility and reactivity (Evangelou *et al.* 1996; Evangelou, 1995) and their investigations have shown that an iron phosphate coating can be established on pyrrhotite thereby eliminating AMD. In one treatment of AMD the oxidation of Fe(II) has been achieved by using an anion exchange resin to which *T. ferrooxidans* was attached. The bacteria oxidise Fe(II) and Fe(III) is precipitated, thereby removing the Fe(III) required to oxidise further pyrite (Umita, 1996). Permeable reactive walls have been used to remove contaminants such as iron, sulfate and heavy metals from AMD by Blowes *et al.* (1998). The use of constructed wetlands for treatment of AMD has also been examined (Fourie *et al.* 1992) and resulted in

improved quality of the effluent due to removal of contaminants such as heavy metals from the mine effluent.

1.3.1.4 Biological controls

The chemistry of the AMD may be influenced by biological activity along the route of leachate migration through the ore. The rate at which pyrite oxidation occurs is influenced by the presence of the iron oxidising bacteria, *T. ferrooxidans*. Biological species can also attenuate the mobility of metals by adsorption or precipitation.

Studies have been done on control of AMD through inhibition of iron oxidising bacteria (Mitchell and Walsh, 1975). At low pH, bacteria such as *T. ferrooxidans* catalyse pyrite degradation by increasing ferrous ion oxidation rates in those regions of the mine or tailings pile which have pH less than 5. *T. ferrooxidans* activity can be inhibited by an increase in ferrous iron concentration. A combinated strategy of increased mine influent ferrous ion concentration with mine sealing may also significantly reduce acidity and the total iron released from working or abandoned coal mines.

1.3.2 Carbonates as chemical controls for acid mine drainage

Carbonates, of which calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are the most common, are the most widely distributed minerals that occur in waste rocks (Kraus *et al*; 1959).

1.3.2.1 Carbonates

Carbonate can consume acid as the soluble phase or as the solid-phase mineral. The simple solution equilibrium of calcite ($CaCO_3$) is

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \quad (-\log K_{so} = 8.42 \text{ at } 25\ ^\circ C) \qquad (1.17)$$

Hydrolysis yields:

If carbon dioxide is dissolved to form carbonic acid, the following reaction occurs:

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \quad (1.19)$$

Assuming equilibrium with atmospheric carbon dioxide, the net result of this reaction is a solution with a pH of about 8.4 and a predominance of bicarbonate ions. Hence, the solution will have the capacity to consume hydrogen ions produced by acid mine drainage.

Acid produced by AMD can be consumed by solid-phase calcium carbonate, a reaction expressed as:

$$2H^+ + CaCO_3 = Ca^{2+} + CO_2 + H_2O \quad (1.20)$$

Under carbonic acid saturated conditions, the loss of carbon dioxide gas is prevented, and bicarbonate ions are formed in solution:

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \quad (1.19)$$

The combined reaction of acid generation from pyrite by air/water oxidation and acid consumption by calcite is described by the following equation:

$$4FeS_2 + 8CaCO_3 + 15O_2 + 6H_2O = 4Fe(OH)_3 + 8SO_4^{2-} + 8Ca^{2+} + 8CO_2 \quad (1.21)$$

Another product formed by reaction of sulfuric acid with calcite is gypsum.

$$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2 \quad (1.22)$$

The susceptibility of calcite to coating or binding by relatively insoluble gypsum and iron salts results in decreased reaction rates, as the reactions have to continue by diffusion through the coatings.

Calcite and dolomite have similar reactions, but siderite (iron carbonate) displays different behaviour and is not acid consuming. Initially, iron is taken into the solution as the ferrous ion:

$$2H^+ + FeCO_3 = Fe^{2+} + CO_2 + H_2O \quad (1.23)$$

In oxidising conditions, oxidation of ferrous iron occurs.

$$4Fe^{2+} + 4H^+ + O_2 = 4Fe^{3+} + 2H_2O \quad (1.24)$$

Ferric iron eventually precipitates and further hydrogen ions are produced.

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (1.25)$$

The net behaviour for the iron carbonate is:

$$4FeCO_3 + O_2 + 6H_2O = 4Fe(OH)_3 + 4CO_2 \quad (1.26)$$

The hydrogen ion addition and removal cancel each other and the net result is ferric iron precipitation.

1.4 BACKGROUND OF THE PRESENT WORK

The research described in this thesis was initially carried out in association with Macraes Mining Company Limited (MMC). It focused on a potential gold mining site on New Zealand's South Island West Coast, with reference to:

- The production of AMD from a proposed mine site.

- The associated production of arsenic species.
- The control of AMD and arsenic at the point of release.
- The impact of AMD on the catchment.

1.4.1 Description and location of proposed mine

At the time of commencement of this thesis MMC was planning the development of a gold mine at it's Globe-Progress prospect, located approximately 6 km southeast of Reefton on the West Coast of the South Island of New Zealand. The location of the proposed development is shown in Fig 1.3. During the course of this work, MMC decided not to proceed with the mine development. However, it is reasonable to assume the mine may be developed in the future, when the economics of gold production becomes more favourable. Hence, details of the proposed mining operation are described.

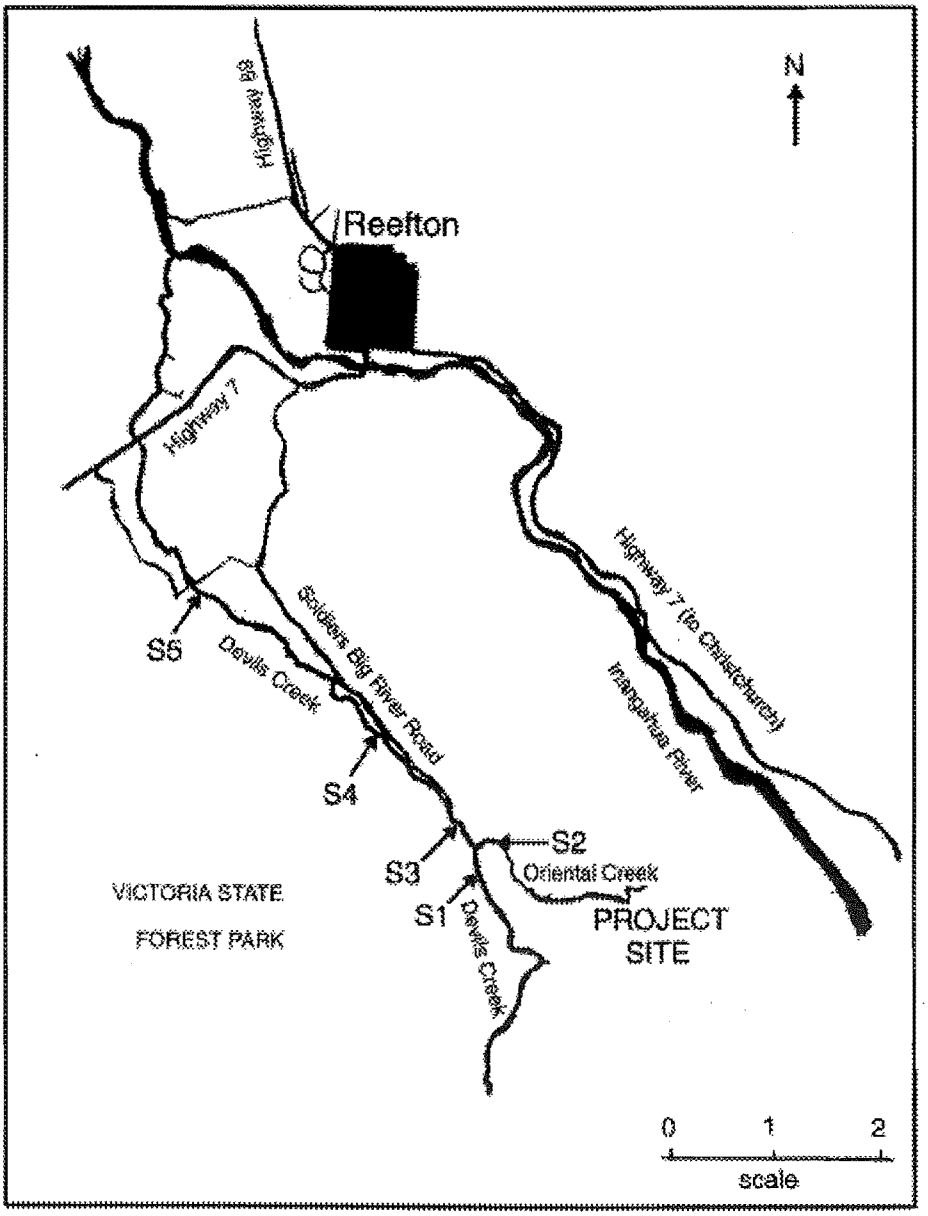
The ore is refractory and the gold occurs within sulfide minerals associated with a large scale shear feature. Arsenic is associated with the mineral of interest (Au), and is found in waste rocks at elevated levels as arsenopyrite, FeAsS.

The ore resource is to be mined at the rate of 5 million tonnes per annum. The open pit will be approximately 800 metres long by 200 metres wide and 200 metres deep and will result in the removal of much of Globe Hill. Once mining is complete, the resulting pit will be backfilled with waste rock.

MMC proposed to process the ore on site by concentration in a flotation circuit, followed by bacterial oxidation and gold extraction by cyanide leaching. The flotation process would result in approximately 4.75 million cubic metres of concentrate residues. It is proposed to dispose off these residues in an onsite tailings storage impoundment located within the upper reaches of the Devils Creek Catchment, approximately 1 km south of the mine.

Approximately 53 million tonnes of waste rock would be generated during the project, which MMC propose to place within the Devils Creek Valley. The waste rock will be placed in a stack immediately downstream of the tailings impoundment embankment in the upper reaches of the catchment (see Figure 1.3).

Figure 1.3: Map of the proposed Globe-Progress prospect on the West Coast of the South Island of New Zealand. The distance scale is in km.



S1-S5 are the sampling sites along the Devils Creek catchment.

1.4.2 Devils Creek catchment and the possible effects of acid mine drainage

The main tributaries in the upper catchment of the Devils Creek are Oriental Creek, Union Creek, and Fossickers Creeks. These are deeply incised, forming steep-sided gullies. In the regional setting, Devils Creek discharges into the Inangahua River approximately 2 km downstream from Reefton. The Inangahua drains into the Buller River, which in turn drains to the Tasman Sea.

The main surface water issues associated with the development of the Globe-Progress gold mine are leaching of arsenic and its effect on the quality of water in Devils Creek.

1.5 SCOPE OF THE PRESENT WORK

Published AMD studies have generally used pure pyrite samples whereas this work has studied waste rocks, which are complex in their characteristics. The mineralogy of the waste rocks (especially acidic sandstone) indicates that they contain pyrite and arsenic as the arsenopyrite.

1.5.1 Objectives

MMC wishes to develop strategies for the treatment of waste rock that reduce the release and hence mobility of arsenic. Therefore this work considered the scenario by which waste rock from the mining is exposed to weathering and the resultant leachate entered the Devils Creek. The results of this work should assist in the formulation of control measures aimed at minimising or even eliminating future arsenic release into Devils Creek.

The work is divided into two sections, (a) the leaching of arsenic from waste rocks and investigation of control measures, and (b) the speciation of arsenic in leachates and its impact on the Devils Creek catchment.

1.5.1.1 Leaching of arsenic from waste rocks and its control.

The objectives in this work were to:

i) Conduct leaching experiments on basic waste rocks (GB 13) and an acid generating sandstone waste rock, representative of the mine site. These included short term (batch) and long term (kinetic) leaching.
ii) Study the effect of leachate pH on the release/mobility of arsenic.
iii) Leach waste rocks under conditions close to those effective at the proposed mining site in Reefton.
iv) Control arsenic solubility and therefore its mobility by the use of limestone layers.

The objectives were achieved by:

i) Examining the effect of Milli-Q, rain and humic water (from local catchment area) on release of arsenic.
ii) Examining the effect of leachate recycling to simulate the movement of acid leachate through the waste body.
iii) Examining the effect of leachate pH on arsenic release by leaching the waste rock under or over a layer of limestone.
iv) Examining the factors effecting the immobilisation of arsenic by use of limestone.

1.5.1.2 Speciation of arsenic in leachates, Devils Creek water and sediments

It is vital to know the baseline levels of arsenic in Devils Creek catchment water and sediments before any anthropogenic input arising from mining activity is initiated. Moreover, it is important to obtain information about the speciation of arsenic as its toxicity is dependent on its chemical and physical form in the water column. The soluble species that arise from leachates can interact with stream sediments.

The objectives were to:

i) Study the speciation of arsenic from waste rocks, in Devils Creek water and in the Creek sediments.

ii) Study the uptake of arsenic by iron oxy/hydroxides, both synthetic and naturally occurring.

iii) Establish the extent of arsenic adsorption to sediments in relation to the possible uptake of arsenic from leachates into Devils Creek sediments.

The objectives were achieved by:

i) Developing a method for the on-site fractionation of arsenic in fresh waters.

ii) Modifying a published method for arsenic fractionation based on FIA and spectrophotometric detection.

iii) Examining the speciation of arsenic and iron released from laboratory leaching experiments on waste rocks and assessing any change in speciation with pH and age of leachate.

iv) Examining the speciation of arsenic in the Devils Creek waters with respect to distance downstream from mine wastes.

v) Assessing the effect of arsenic adsorption onto Devils Creek sediments and synthetic sediments at conditions effective under AMD.

vi) Assessing the competitive effects of humic and fulvic acids and elevated levels of sulfate and calcium on arsenic uptake to synthetic iron hydroxides.

vii) Determining the major arsenic species (phase) in the Devils Creek sediments by use of appropriate chemicals extractants to selectively extract arsenic from the sediments.

CHAPTER 2

EXPERIMENTAL

2.1 CLEAN ROOM PROTOCOLS

With the exception of arsenic measurements by FIA (2.3.11), flame atomic absorption spectroscopy (2.3.5), column leaching (Chapter 7), batch leaching and uv-visible spectrophotometry (2.3.2), all manipulations and measurements were made in the positive pressure class 100 clean room. These were conducted while clad at all times with lint-free polyester overcoat, hat, overshoes, and disposable plastic gloves. Most manipulations in which samples were exposed to the atmosphere were carried out within a laminar-flow workbench inside the clean room, and care was taken at all times to remain downstream of the samples in the clean airflow. All equipment in the clean room that came in direct contact with the samples was either glass or polyethylene, which was pre-washed with 1% HNO_3 (BDH-Aristar) then rinsed with Milli-Q water.

Micropipettes were used to measure and deliver microliter volumes. This was done using four different sizes of Gilson Pipetteman™ micropipettes, which were, P20 (2-20 μL), P100 (20-100 μL), P200 (50-200 μL), and P1000 (200-1000 μL). Micropipette tips specifically designed for use with the Gilson micropipettes were used directly without the need for pre-cleaning.

2.2 MATERIALS

2.2.1 Water

All stock and working solutions were prepared with high purity Milli-Q water. This was prepared by passing distilled water through exchange resins in a Milli-Q® (Millipore) water purification system. This involved removal of organic, metal and anion impurities, by sequentially passing distilled water through a Super-C carbon cartridge, Ion-ex anion and cation exchange cartridges, an Organex-Q cartridge and finally a Millipak® 0.22 μm pore size filter. The Organex-Q cartridge removes organics by adsorption to activated carbon.

2.2.2 Volumetric glassware

All vessels (i.e. glassware and plastic containers) for use in solution and sample storage or preparation were extensively cleaned, initially by washing in detergent then soaking in 10% HNO_3 (BDH-Analar) for several days. For use in the clean room, this was followed by immersing in 1% HNO_3 (BDH-Aristar) overnight in the clean room. Between each acid cleaning step and before use, the vessels were thoroughly (5-8 times) rinsed in Milli-Q water.

2.3 METHODS

2.3.1 Conductivity, pH, dissolved oxygen and redox potentials

2.3.1.1 Conductivity

Conductivity of leachate solutions was measured with a conductivity meter (EDT-RE387Tx Microprocessor Conductivity Meter). These gave the resistivity of ions in solutions and therefore information on the ionic strength. The conductivity probe was

calibrated against standard solutions of 0.01 M and 0.1 M KCl (BDH-Analar). Solution resistivity calibrations were adjusted to compensate for temperature variations.

2.3.1.2 pH

Field measurements of fresh water samples were made using a Lutron PH 206 portable meter. Measurements in the laboratory were made with a Russell CMAWL/4/5/S7 micro-combination electrode coupled to a PHM64 pH meter (Radiometer, Copenhagen). Natural waters typically have low ionic strength, therefore the electrodes were calibrated against dilute buffers (Covington *et al.* 1983). The dilute buffers were 0.01 M phthalate (pH 4.12 at 25 °C) and 0.0025 M phosphate (pH 7.07 at 25 °C). Compensation in pH was made for changes in temperature.

2.3.1.3 Dissolved oxygen

Dissolved oxygen in anoxic leaching experiments was monitored using a Beckman Fieldlab Oxygen Analyser. The oxygen probe for this instrument was calibrated using deoxygenated and oxygen saturated Milli-Q water solutions. Deoxygenated Milli-Q water was prepared by purging with commercial 'O_2-free' nitrogen gas, from which trace amounts of oxygen were removed by bubbling through an acidic vanadous (V^{2+}) solution. The vanadium solution was prepared by the reduction of acidic (H_2SO_4) vanadyl sulfate by zinc amalgam (Russell, 1977).

A zinc amalgam was prepared by stirring a 2% mercuric chloride solution with zinc pellets for 20 minutes. The amalgam was rinsed four times with Milli-Q water. A $VOSO_4$ solution was prepared by dissolving 2.5 g of $VOSO_4.2H_2O$ (BDH laboratory reagent) in Milli-Q water. Concentrated H_2SO_4 (7 mL, BDH-Analar) was added and the mixture diluted to 250 mL. The amalgam was placed in a gas bubbler and covered with acidic $VOSO_4$ solution. On bubbling N_2 through the zinc amalgam/$VOSO_4$ the colour of the solution was observed to change from blue (VO^{2+}) to green (V^{3+}) to violet (V^{2+}). The vanadous solution was stored in the gas bottle under N_2 gas.

2.3.1.4 Redox potentials

Redox potentials (E) were measured with a platinum foil electrode, relative to an Ag/AgCl electrode, coupled to a PHM64 pH meter (Radiometer, Copenhagen). The reference electrode was calibrated with an equimolar solution of 0.020 M Fe(II)/Fe(III). The equimolar Fe(II)/Fe(III) solution was prepared by dissolving 0.66 g of $K_3Fe(CN)_6$ (BDH-Analar) and 0.84 g $K_4Fe(CN)_6.3H_2O$ (BDH-Analar) then making up to 100 mL with 1 M H_2SO_4 (BDH-Analar) in Milli-Q water ($E_{Fe(CN)_6^{2-}/Fe(CN)_6^{3-}}$ = 450 V vs. SCE). Where appropriate, the E was converted to E_h (mV vs. SHE) by adding 249 mV to the measured E.

2.3.2 Fe(II) analyses by uv-visible spectrophotometry

Ferrous iron was measured as the red-orange iron (II)-orthophenanthroline complex at 508 nm using an uv-visible spectrophotometer (GBC - 918), according to the procedure outlined in Skoog and West (1985).

Orthophenanthroline, which is a weak base, exists as the phenanthrolinium ion ($PhenH^+$) in acid solutions. Formation of the red-orange iron (II)-orthophenanthroline complex is represented by the equation below.

$$Fe^{2+} + 3PhenH^+ \text{ ----------> } Fe(Phen)_3^{2+} + 3H^+ \qquad (2.1)$$

For the determination of total iron, 5 % ascorbic acid was included to reduce Fe(III) (instead of hydroxylamine/hydroquinone applied in the Skoog and West (1985) method). The complex was very stable following 10 minutes of colour development. Absorbances due to Fe(II) in the samples were compared against similarly treated standard 0-5 ppm Fe^{2+} solutions.

a) Preparation of reagents

i) Standard iron solution (0.01 mg/mL) was prepared by weighing 0.0702 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ (BDH-Analar) into a 1 L volumetric flask. This was dissolved in 50 mL of Milli-Q water containing 2 mL of concentrated H_2SO_4 (BDH-Analar) then diluted to 1 L.

ii) Orthophenanthroline solution was prepared by dissolving 0.1 g of orthophenanthroline monohydrate (BDH-Analar) in warm Milli-Q water, cooling, then making up to 100 mL. The solution was stored in the dark.

iii) Sodium acetate solution was prepared by dissolving 10 g of CH_3COONa (BDH-Analar) in 100 mL of Milli-Q water.

iv) Ascorbic acid (5 %) was prepared by dissolving 5 g of commercial ascorbic acid in 100 mL of Milli-Q water.

2.3.3 Total iron measurements by electrothermal atomic absorption spectrometry

Total Fe measurements in 0.025 μm membrane filtered and unfiltered samples were performed using the microprocessor-controlled graphite furnace atomic absorption spectrometer (GBC - 908A). The Fe absorbance was measured at 248.3 nm, using a lamp current of 7 mA and a 0.2 nm slit. The instrument parameters, graphite furnace and furnace sampler programs used are shown in Table 2.1a-c. A stock solution of 10 ppm Fe^{2+} was prepared from ferrous ammonium sulfate (Merck) in 0.1 M H_2SO_4 (BDH-Aristar). This stock solution was diluted to a working concentration of 20 ppb Fe in 1% HNO_3 (BDH-Aristar). The calibration was effected using a series of standards (0-20 ppb Fe) prepared by auto dilution according to the furnace sampler program. Fe in the samples was quantified by comparison against the standard calibration solutions.

Table 2.1: Furnace Sampler program for total Fe determination by GFAAS

a) Instrument Parameters

System Type	Furnace
Element	Fe
Matrix	HNO_3
Lamp Current (mA)	7.0
Wavelength (nm)	248.3
Slit Width (nm)	0.2
Instrument Mode	Absorbance BC on
Sampling Mode	Auto Sampling

b) Graphite Furnace parameters

Step	Final Temp (°C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal graphics
Step 1	95	1	1	Inert	Off	Off
Step 2	110	10	15	Inert	Off	Off
Step 3	150	5	10	Inert	Off	Off
Step 4	600	15	5	Inert	Off	Off
Step 5	600	0	2	None	Off	Off
Step 6	2300	1.0	2	None	On	On
Step 7	2400	0.1	1	Inert	Off	On

c) Furnace Sampler Parameters

Standards Preparation	Auto-mixed
Sample Injections	1
Inject Before Step No.	1
Sample Dry to Step No.	1
Injection Speed	4 (μL/s)
Recalibration Rate	10
Rescale Rate	5
Rescale Standard No.	3

2.3.4 Arsenic speciation measurements using electrothermal atomic absorption spectrometry

Trace amounts of As(III) and As(V) were measured by hydride generation atomic absorption spectroscopy. This method involved generating arsine gas (AsH_3), and collecting it on pre-deposited palladium in a graphite furnace, followed by the atomisation and measurement of arsenic. Measurements were made on waste rock leachates and sediment extracts (Chapter 8) and fresh water samples (Chapter 4).

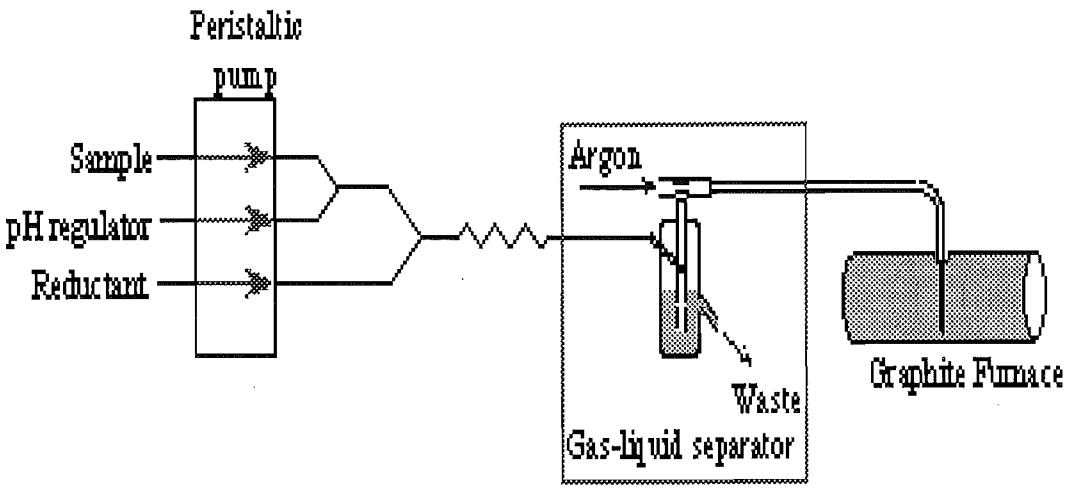
a) Electrodeposition instrumentation

A Pd modifier was coated onto the graphite furnace by *in-situ* electrodeposition. The power supply for electrodeposition was a GBC EPS 2000 current-voltage regulator. This was capable of producing 0-20 V (DC) and a current of 0-100 mA from a 230 V AC power supply. An auto sampler probe was constructed of 6 cm Pt/Ir capillary connected to the PTFE tubing on the autosampler arm. The Pt/Ir capillary and the furnace were connected to the DC power. This allowed for electrodeposition using the Pt/Ir capillary as the anode and the pyrolytic graphite furnace as the cathode. Optimum current flow (5-20 mA, 2-3V) was achieved by adjusting the probe penetration into the furnace, such that the probe was separated from the bottom of the graphite tube by *ca.* 0.6 mm. The potentials and currents in the graphite furnace electrodeposition were measured using digital multimeters (Dick Smith Q-1442).

b) Hydride generator

A GBC HG 3000 hydride generator was used to produce arsine. The hydride generator incorporates a flow manifold with a gas liquid separator as shown in Figure 2.1. The resulting arsine was carried to the furnace in an argon carrier gas for accumulation on electrodeposited palladium. Samples of arsine were introduced into the graphite furnace via a PTFE tube for a specified period (20 seconds). To account for the time required for passage of arsine through the tube between the hydride generator and the furnace (46 seconds) the hydride generator was started ca. 60 seconds before the accumulation period was initiated. The following diagram shows the flow manifold on the hydride generator.

Figure 2.1: The flow manifold on the GBC HG 3000 hydride generator



c) Reagents

The following reagents were prepared to conduct hydride generation, electrodeposition of palladium and the determination of arsenic species.

As(III) determination

i) A 10 ppm palladium working solution was prepared by diluting 0.5 mL of a 500 ppm Pd^{2+} working stock (in 5% Aristar HNO_3) into a 25 mL volumetric flask using 0.1% HNO_3 diluent.

ii) A 0.5 M acetate buffer was prepared by dissolving 40 g of sodium acetate (BDH-Aristar) to 875 mL of Milli-Q water. An isopiestic distilled acetic acid solution was added until a pH 5.0 was attained. The buffer was then made up to 1L with Milli-Q water.

iii) A working solution of 0.04 M $NaBH_4$ (in 0.0375 M NaOH) was prepared by dissolving 1.5 g of $NaBH_4$ (BDH-Analar) and 1.5 g of NaOH (BDH-Analar) then making up to 1 L with Milli-Q water. This solution was prepared fresh each time arsenic measurements were made.

iv) Samples for As(III) determination were made up to 50 mL and acidified with HCl (BDH-Aristar) to 1% v/v. Arsenite standards (0-10 ppb) were treated similarly. A sample volume of 50 mL was required to obtain triplicate measurements by hydride generation.

v) A stock solution of As(III) (1000 μg/mL) was made by dissolving 0.066 g of As_2O_3 (BDH-Analar) in 1.25 mL of 1 M NaOH (BDH-Analar). Milli-Q water was added to about 25 mL, then 6.6 mL of 30 % HCl (BDH-Analar) was added and the solution was made up to 50 mL with Milli-Q water. Appropriate dilutions were made to prepare working standards.

As(V) and total arsenic determination

For arsenate and total arsenic measurements, 1% L-cysteine was added to the acidified sample in the 50 mL volumetric flask at least 10 minutes prior to the borohydride reduction. Arsenate standards (0-10 ppb) were also treated in this manner.

i) A stock solution of As(V) (1000 μg/mL) was made by dissolving 0.2082 g of $Na_2HAsO_4.7H_2O$ (BDH-Analar) in 6.6 mL of 30 % HCl (BDH-Analar) then the solution was made up to 50 mL with Milli-Q water. Appropriate dilutions were made to prepare working standards.

2.3.4.1 ETAAS experimental protocols

a) Palladium electrodeposition and arsenic determination

The modifier (20 μL of 10 ppm palladium nitrate solution in 0.1% v/v HNO_3) was injected into a graphite furnace. Deposition was effected for 20 seconds at 45 °C, at a cell potential of 2.0 V ($E_{cell} = E_{anode}-E_{cathode} + iR$). The modifier was dried at 150 °C. Arsine gas (AsH_3) was produced in the hydride generator in which the sample or standard was mixed with a pH buffer (acetate at pH 5.0) and the resulting solution merged with a 0.04 M $NaBH_4$ (in 0.05M NaOH) solution. Arsine was accumulated in the furnace at 300 °C

for 20 seconds. The furnace temperature was then ramped to 2400 °C to atomise the arsenic and the absorbance was measured at 193.7 nm. The autosampler program was used to control the deposition of palladium whereas sample introduction was controlled manually. Total As was measured following pre-reduction of As(V) to As(III) with 1% L-cysteine (BDH) in 1% HCl (10 min). As(V) was calculated by difference.

The instrument, graphite furnace and furnace sampler programs used are shown in Table 2.2.

Table 2.2: Furnace Sampler program for arsenic determination by GFAAS

a) Instrument Parameters

System Type	Furnace
Element	As
Matrix	Arsine gas
Lamp Current (mA)	8.0
Wavelength (nm)	193.7
Slit Width (nm)	1.0
Slit Height	Reduced
Instrument Mode	Absorbance BC on
Sampling Mode	Manual Sampling

b) Graphite Furnace Parameters

Step	**Final Temp** (°C)	**Ramp Time** (s)	**Hold Time** (s)	**Gas Type**	**Read**	**Signal Graphics**
Step 1	45	0.1	0.0	Inert	Off	Off
Step 2	110	10.0	10.0	Inert	Off	Off
Step 3	150	10.0	15.0	Inert	Off	Off
Step 4	300	5.0	30.0	None	Off	Off
Step 5	150	2.3	10.0	None	Off	Off
Step 6	2400	1.2	2.0	None	On	On
Step 7	2400	0.1	2.0	Inert	Off	Off

c) Furnace Sampler Parameters

Standards Preparation	Pre-Mixed
Sample Injections	1
Inject Before Step No.	1
Sample Dry to Step No.	1
Injection Speed	4 (μL/s)
Recalibration Rate	0
Rescale Rate	0
Rescale Std. No.	3

2.3.4.2 Interferents

Calcium and iron were the major matrix components in the samples that were being analysed for arsenic. These components arose from the leaching of waste rocks in the presence (Ca) or absence (Fe) of limestone. The concentrations of calcium and iron used in interference studies were similar to levels in the final leachates. The experimental method was checked for calcium and iron interference on the formation of arsine. Arsine generation from standard solutions of As(V), the reductant (L-cysteine) and Ca^{2+} (20-600 ppm) was compared with that from arsenate solutions and L-cysteine alone (without Ca^{2+}). The potential of Ca^{2+} to interfere with the generation of arsine from As(III) was also investigated. Similarly the method was investigated for possible interference by iron (1-50 ppm). Results showed that calcium and iron did not interfere measurably.

2.3.5 Flame atomic absorption spectroscopy

Leachate samples containing ppm levels of calcium and iron were analysed by flame atomic absorption spectroscopy in an air-acetylene flame. This was done using a Varian AA – 1475 flame atomic absorption spectrometer. Calcium was measured at 422.7 nm, using a 4 mA lamp current with a slit width of 0.5 nm. Fe was measured at 248.3 nm, using a slit width of 0.5 nm and a lamp current of 5 mA. The elements were quantified in the samples by direct comparison against standard Ca^{2+} (0-10 ppm) and Fe^{2+} (0-40 ppm) solutions.

2.3.6 Square wave anodic stripping voltammetry (SW-ASV) instrumentation and method

All analyses of the metals Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} were made by SW-ASV. These analyses used the PAR 303A hanging mercury drop electrode, a reference electrode (Ag/AgCl in a 3 M KCl solution) and a counter electrode (Pt) coupled with a microprocessor controlled polarographic analyser (EG & G Princeton Applied Research, model 348B) and a DMP-40 plotter. Analytical solutions (10 mL) were held in a glass cell. Routinely used instrumental parameters are listed in Table 2.3.

Table 2.3: Typical instrumental parameters for SW-ASV by the 384B Polarographic Analyzer

Mode	SWV
Initial Potential	-1.200 V
Final Potential	0.200 V
Purge	600 Seconds
Condition	30 Seconds
Condition Potential	0.250 V
Deposition Time	600 Seconds
Equilibration Time	15 Seconds
Cycles	1
Scan Increment	2 mV
Frequency	100
Pulse Height	0.020 V
Replications	1
Standard Curve	
Tangent Fit	Yes
Peak Location	Yes

For all ASV analyses the stripping currents (nA) were obtained from peaks heights at voltages approximating to each metal's half wave potential ($E_{1/2}$). These peaks were quantified by standard addition, when the samples were spiked with known concentrations of the metal ion of interest. SW-ASV labile metals in the leachate samples were determined after filtering (0.025 μm) and adding KNO_3 (BDH-Aristar) to give a final concentration of 0.05 M.

2.3.7 Ion chromatography

Sulfate was measured by ion chromatography using a Dionex-100 Chromatograph, and an Ion Pac AS4A-SC (4 mm diameter) anion separation column. Detection of the separated sulfate ion was made using a conductivity detector (CD-20) and the chromatograms recorded on an integrator (Dionex 4400). Retention time of sulfate ions in the column was ~ 8 minutes.

The eluant was a solution composed of 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate, prepared by weighing 0.19 g of Na_2CO_3 and 0.14 g of $NaHCO_3$ then dissolving and making up to 1 L with Milli-Q water. Working solutions of SO_4^{2-} (0-100 ppm) were prepared from a stock solution of 200 ppm SO_4^{2-}. The stock solution was prepared by dissolving 0.148 g of Na_2SO_4 (BDH-Analar) and making up to 50 mL with Milli-Q water.

The linear calibration range for this method was 0-200 ppm, with a DL of 0.06 ppm (3σ for a 0.20 ppm solution).

2.3.8 Speciation calculations

Speciation calculations were performed with the program SPECIES contained in the SolEq computer program (Pettit and Powell, 1999). The IUPAC Stability Constants Database (Pettit and Powell, 1997) and literature sources were consulted for the appropriate complexation, hydrolysis and protonation constants. Where stability constants at a particular ionic strength were not available, the Davies Equation in the SolEq program was used to adjust selected constants to the required ionic strength.

2.3.9 Natural organic matter (NOM)

NOM in water samples was measured on 0.025 μm membrane filtered samples. It was determined by measurement of UV absorbance at 360 nm using a GBC UV/VIS 918

spectrophotometer, and a 1 cm cell. The NOM concentration (g/m^3) was calculated from the empirical equation (Collier, 1987):

$$NOM\ (g/m^3) = 59.6\ Abs\ (1\ cm) + 1.9$$

The experimental procedure for the XAD-4 isolation of NOM bound to iron is described in 3.3.1.

2.3.10 Mossbauer spectroscopy

Mossbauer spectroscopic measurements were done in house to determine the oxidation state of iron in limestone samples obtained from Mt Somers limestone quarry. These were provided by Dr. C. Ternant and were made on an Elscint Mossbauer function generator (model MFG-N-5) instrument.

2.3.11 Arsenic speciation by flow injection analysis

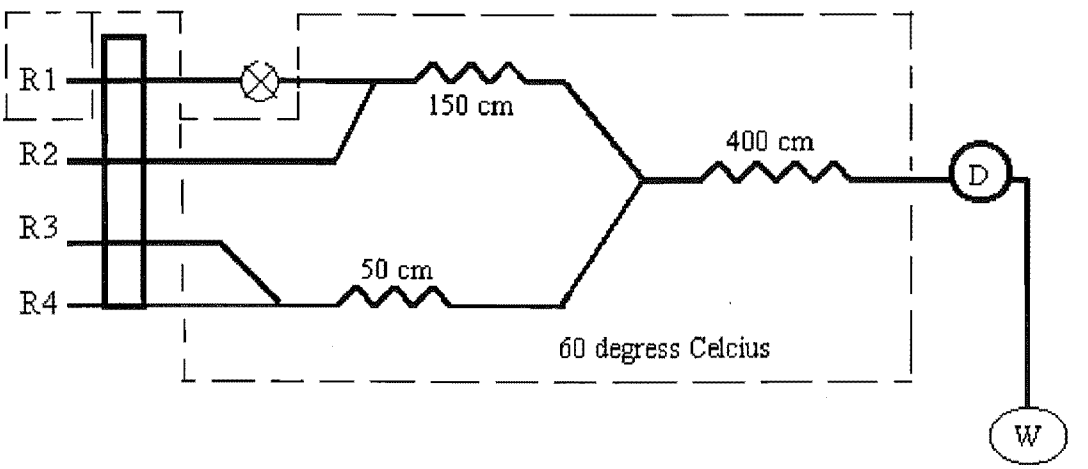
The reaction of arsenate with an acidic solution of sodium molybdate dissolved in acid solution leads to the formation of a heteropolyacid, $H_3[AsMo_{12}O_{40}]$. This reaction was effected by flow injection analysis. The method is based on the formation of the heteropoly acid at 60 °C (Linares *et al.* 1986) and spectrophotometric detection at 820 nm. Arsenite is oxidised to arsenate by iodate to effect its determination by this method. Improvements included during method development are described in 3.2 and results of arsenic speciation measurements are given in Chapter 7. This method is suitable for arsenate concentrations in the range 0.2-1.5 ppm and was applied to the determination of arsenate and arsenite generated in column leaching experiments. The following section presents the final method adopted.

a) Apparatus

Figure 2.2 shows the FIA manifold developed in this work. It was adapted from Linares *et al* (1986). As indicated, the majority of the manifold was in a thermostatted water bath (60 °C).

Components used in the FIA manifold included a computer controlled GBC – 918 uv-visible spectrophotometer with a 10 mm × 3mm flow cell, an Ismatec (IPS-12) 12 channel peristaltic pump, a laboratory built sample injection valve, and water bath with a thermostatic controlled heater (Tecam).

Figure 2.2: The FIA manifold for the determination of arsenate and total inorganic arsenic by the modified molybdenum blue method.



Where R1 = H_2O (*1.85 mL* min^{-1})

R2 = H_2O or 0.035 M KIO_3 or 3 M H_2SO_4 (*0.44mL* min^{-1})

R3 = 10 % ascorbic acid (*0.44 mL* min^{-1})

R4 = 0.10 M MoO_4^{2-} + 6.16 x 10^{-5} M $KSbO.C_4H_4O_6$ (*0.44 mL* min^{-1})

Sample loop volume = 240 µL, D = detector (820nm), W = waste.

b) Arsenate and arsenite measurements

- Arsenate (AsO_4^{3-}) was determined with R2 = H_2O. Under these conditions PO_4^{3-} also contributes to the signal.
- The amount of PO_4^{3-} was determined with R2 = H_2SO_4
- (only PO_4^{3-} gives a signal).
- Arsenite, AsO_2^-, was determined after oxidation to AsO_4^{3-} with KIO_3. For R2 = KIO_3, the signal corresponds to the sum of AsO_4^{3-} and AsO_2^-, hence AsO_2^- was calculated by difference.

Calibration curves were required for AsO_4^{3-} with R2 = H_2O and R2 = KIO_3 because the sensitivity for AsO_4^{3-} is different in each case. The adapted procedure involved establishing calibration curves for AsO_4^{3-} (R2 = H_2O), AsO_4^{3-} (R2 = KIO_3), AsO_2^- (R2 = KIO_3), PO_4^{3-} (R2 = H_2SO_4) and PO_4^{3-} (R2 = H_2O). Calibration curves were obtained daily prior to measuring the samples.

The detection limit (DL) for arsenate was 0.33 μM, and the working range was 2 - 10 μM. Higher arsenic concentrations were measured by decreasing the sample loop volume.

c) Reagents

i) A 0.15 M sodium molybdate solution in 3.38 M HNO_3 and 12.5% glycerol was prepared from 3.554 g of $Na_2MoO_4.2H_2O$ (BDH-Analar), 12.5 g of glycerol (BDH-Analar) and 10.75 mL of HNO_3 (BDH-Analar), made up to 100 mL with Milli-Q water.

ii) An ascorbic acid (10%) solution was prepared daily by weighing 10 g of ascorbic acid (commercial grade), adding 10 g of glycerol (BDH-Analar) then making up to 100 mL with Milli-Q water.

iii) Potassium iodate solution (0.035 M) was prepared by weighing 0.36 g of laboratory reagent grade KIO_3 (Ajax chemicals) and dissolving in 50 mL of Milli-Q water. This solution was prepared daily.

iv) A 3 M sulfuric acid solution was prepared by measuring 81.6 mL of H_2SO_4 (ρ = 1.84) (BDH-Analar) then adding slowly with stirring to about 400 mL of Milli-Q water, then making up to 500 mL.

v) Antimony potassium tartrate solution (3.08×10^{-4} M) was prepared by weighing 0.005g of $KSbO.C_4H_4O_6$ (BDH-Analar) then making up to 50 mL with Milli-Q water. This solution was freshly prepared daily.

vi) A working solution consisting of molybdate and antimony potassium tartrate solution was prepared by mixing solutions (i) and (v) at a 4:1 volume ratio. This dilution gave a working concentration of 0.10 M for sodium molybdate. Solutions of this working mixture were prepared daily.

vii) Stock solutions of 1.0×10^{-2} M arsenate and arsenite were prepared. The arsenate solution was prepared by weighing 0.7800 g of sodium arsenate heptahydrate (BDH-Analar) then making up to 250 mL with Milli-Q water. The arsenite solution was prepared by weighing 0.2598 g of sodium arsenite ($NaAsO_2$-Sigma) then making up to 200 mL with Milli-Q water. Both arsenic stock solutions were prepared in 1% HCl (BDH-Analar). A stock solution of 1.0×10^{-2} M PO_4^{3-} was prepared by weighing 0.6805 g of KH_2PO_4 (BDH-Analar) and making up to 500 mL.

2.3.12 Fresh water sampling and preservation

In order to measure the current arsenic speciation in the Devils Creek catchment, water samples were collected using 1 L polyethylene plastic bottles from various sites downstream from the proposed mine waste site. Samples were acidified to pH 2.0 using HCl (BDH-Aristar) and stored in a cooler for transport to the laboratory. Less than 24 hours after collection, the samples were stored in a fridge at 4 °C.

a) Selection of sample sites

Samples were collected from five sampling sites (See map in Chapter 1).

i) Site 1 was located at the upper Devils Creek, the closest to the source of leachates from the proposed mine.

ii) Site 2 was at the upper Oriental Creek.

iii) Site 3 was at confluence of Devils and Oriental Creeks

iv) Site 4 was located 2 km downstream from the confluence of Devils and Oriental Creeks.

v) Site 5 was 4 km downstream from the confluence of Devils and Oriental Creeks.

Three water samples and one sediment sample were collected from each site. One water sample from each site was acidified to pH 2.0 with HCl (BDH-Aristar) and stored for total As and Fe analysis.

b) On-site fractionation of arsenic

Water samples were sequentially passed through XAD-4 and Chelex-Fe(III) resins to fractionate arsenic on site. The separated fractions were acidified to pH 2.0 with HCl (BDH-Aristar) and stored. The preparation and description of XAD-4 and Chelex-Fe(III) resins are described in Chapter 3. Arsenic results by these fractionation methods are shown in Chapter 7

2.3.13 Sequential extraction of arsenic from Devils Creek sediments

Sediments collected from the Devils Creek catchment were initially wet sieved to –64 μm, and dried in an oven at <50 °C. For determination of total As by HG-GFAAS and of Fe, Mn, Al and Ca by ICP, sieved sediments (1g) were digested with 20 mL of concentrated HNO_3 + 10 mL HCl acid mixture and made up to 50 mL. To characterise the major phases responsible for As adsorption/occlusion, 1 g samples of –64 μm sediments were treated by a sequential series of extractant solutions according to the methods by Chunguo and Zihui (1988), and Lum and Edgar (1983). Each extraction step involved 10 mL of extractant.

i) **As(III) and total soluble As**: Shake for 5 hours with Milli-Q water.

ii) **Loosely bound As**: Shake residue fraction from (i) with 1.0 M NH_4Cl (BDH) for 5 hours.

iii) **Aluminum arsenate**: Wash the residue from (ii) twice with a saturated solution of NaCl (BDH-Analar) and shake with 0.5 M NH_4F (BDH-Analar) for 5 hours.

iv) **Manganese oxides bound arsenate**: Extract the residue from (iii) for 30 min with a mixture of 0.1 M hydroxylamine hydrochloride (Ajax-Analar) and 1.0 M ammonium acetate (BDH-Analar), adjusted to pH 6 with HCl (BDH-Analar).

v) **Iron arsenate**: Wash the residue from (iv) twice with a saturated solution of NaCl (BDH-Analar) and shake with 0.1 M NaOH (BDH-Analar) for 17 hours.

vi) **Calcium arsenate**: Wash the residue from (v) twice with a saturated solution of NaCl (BDH-Analar) and shake with 0.5 M sulfuric acid (BDH-Analar) for 5 hours.

vii) **Iron occluded As**: Wash the residue from (vi) twice with a saturated solution of NaCl (BDH-Analar) and react with 0.3 M Na-citrate (BDH-Analar) and 0.5 g of $Na_2S_2O_6$ (BDH-Analar) at 90 °C.

viii) **Organic bound As**: React the residue from (vi) with H_2O_2 at 90 °C for 5 hours and extract the residue with 1.2 M NH_4OAc (BDH-Analar)/20%HCl (BDH-Analar).

After each step the extraction mixtures were centrifuged at 2500 rpm for 15 minutes, the supernatants removed, made up to 25 mL volume and filtered through a 0.025 μm membrane filter. Arsenite and arsenate were measured in the filtrates using hydride generation atomic absorption spectrometry.

2.3.14 Sandstone and GB 13 waste rock samples

Waste rock samples of acidic sandstone and a basic waste rock labeled GB 13 were supplied by the Macraes Mining Company in 1996. Before supply of these rock samples, they were crushed to ≤ 10 mm particle size. These waste rock types represented the variation in waste rocks containing arsenopyrites, of which sandstone has a relatively

high arsenic content. Descriptions of the characteristics of the waste rocks and their leachates are in Chapter 5.

2.3.15 Limestone samples

Limestone was used in tests to control leachate acidity and the solubility of arsenic species derived from the mine waste rocks. Macraes Mining Company supplied one limestone sample and the other was selected from the Mt Sommers limestone quarry. Analytical results for these are given in Chapter 8.

2.3.16 External analyses

Samples of limestone and mine waste rocks were sent to various locations outside of the Chemistry department for analyses. Samples were solids, acid digests, leachates or fresh water samples, as required for analyses by the particular analytical methods. The external analyses were done by: inductively coupled plasma atomic emission spectroscopy, X-ray fluorescence, petrographic examination and X-ray powder diffraction.

2.3.16.1 Inductively coupled plasma atomic emission spectroscopy

Inductively coupled plasma atomic emission spectroscopic (ICP-AES) determinations for minor elements were performed at the ICP facility at AgResearch in Palmerston North, New Zealand. Fresh water samples from Devils Creek were analysed directly. Samples of sediments (Devils Creek), GB 13 and sandstone waste rocks (1 g) and limestone (1g) from Macraes Mining Company, and Mt Somers Limestone Quarry, were digested with a 1:1 mixture of HCl (BDH-Aristar) and HNO_3 (BDH-Aristar) before dispatch for analyses.

2.3.16.2 X-Ray Fluorescence

Solid samples of limestone, GB 13 and sandstone waste rocks were sent to the Geology Department, University of Canterbury, for X-ray fluorescence analyses of the major and minor elements. Results for these are shown in Chapter 6.

2.3.16.3 Petrographic examination

Samples of the waste rocks GB 13 and sandstone were submitted to the Institute of Geological & Nuclear Sciences Limited (IGNS), in Lower Hutt, New Zealand to obtain petrographic and mineralogical information. Details provided by IGNS gave information on the mineralogical composition, sulfide, arsenic sulfide and the carbonate mineral content of the waste rocks. The results are summarised in Chapter 6.

2.3.16.4 X-ray powder diffraction

X-ray powder diffraction measurements were made on fractions of the sandstone sample by Dr Cyril Childs (Chemistry Department, Victoria University) using the facilities at Landcare Research Ltd, Palmerston North.

CHAPTER 3

ARSENIC SPECIATION: METHOD DEVELOPMENT

3.1 INTRODUCTION

3.1.1 Arsenic speciation

Chemical speciation analysis is defined as the determination of the individual concentrations of the various chemical or physical forms of an element which together make up the total concentration of that element in a sample (Batley and Florence, 1980; Batley and Florence, 1988). This implies that any element (e.g. arsenic) may exist in different physico-chemical forms in any natural system. These could exhibit different physical, chemical and biological properties (Patterson and Passino, 1987). No meaningful interpretation of either biological or geochemical processes can be made without speciation information (Florence, 1983).

Arsenic in environmental systems exists mainly as As(V) and As(III), with minor amounts of methylated species. Of these As(III) is the most toxic form. Inorganic arsenic species (As(V) and As(III)) are also present in anthropogenic systems such as leachates derived from mine waste rocks containing arsenopyrite. Detailed discussions devoted to the speciation of arsenic are presented in Chapter 1. In this research, the speciation of arsenic was of interest. Data on arsenic speciation were needed to assist in formulating control measures aimed at minimising or even eliminating future arsenic release from the proposed waste rock dump site at Reefton. Therefore, analytical methods were developed to measure arsenic speciation in surface waters and leachates. A field method was

developed for the on-site fractionation of arsenic in fresh waters using XAD-4 and Chelex-Fe(III) resins. Fractionation in the field alleviates the problem of changes in speciation during transport and storage for analysis in the laboratory.

3.1.2 Techniques for arsenic fractionation

Various analytical techniques are available for arsenic speciation in aqueous samples. These may include spectrophotometric methods such as the method applied in this work (Linares *et al.* 1986), electroanalytical, and hydride generation atomic absorption spectrometry methods.

The reaction of arsenate with an acidic solution of sodium molybdate dissolved in acid leads to the condensation of molybdate and arsenate ions (catalysed by antimony) by a process of oxygen sharing to give the heteropolyacid, $H_3[AsMo_{12}O_{40}]$. This consists of a molybdate "cage" about a central tetrahedral AsO_4^{3-} nucleus. Partial reduction of the Mo(VI) to the Mo(V) by ascorbic acid leads to the intense blue colouration of the heteropolyacid. The colour is associated with a charge transfer between molybdenum ions in different oxidation states. The absorbance is proportional to the concentration of AsO_4^{3-} in the sample. Linares *et al* (1986) developed a FIA spectrophotometric method for arsenic speciation in aqueous samples based on the heteropolyacid, $H_3[AsMo_{12}O_{40}]$. The method was effective for the determination of arsenate. Arsenite was measured by prior oxidation with iodate. Phosphate and arsenate were measured simultaneously, but by merging the sample with an acidic reagent stream it was possible to determine phosphate alone (no arsenate signal). This method was exploited in this work.

Electroanalytical methods include direct classical dc polarography (Meites, 1954), and indirect polarographic measurements on 12-molybdoarsenic acid (Barrado *et al.* 1990). Differential pulse polarography (DPP) at the dropping mercury electrode (DME) (Henry *et al.* 1979), the static mercury drop electrode (SMDE) (McCory-Joy *et al.* 1982) and the hanging mercury drop electrode (HMDE) (Myers and Osteryoung, 1973; Henry and Thorpe, 1980; Reed and Stolzberg, 1987; Barbera *et al.* 1989) have also been used.

Stripping techniques include differential pulse anodic stripping voltammetry (DPASV) (Forsberg *et al.* 1975), anodic stripping voltammetry (ASV) using a gold-coated electrode (Forsberg et al. 1975; Davis et al.1978; Florence *et al.* 1980; Lee and Meranger, 1981) and DPASV at a rotating gold disc electrode (Estaban *et al.* 1994). Cathodic stripping voltammetry (CSV) at a HMDE has also been used to determine arsenic (Zima and van den Berg, 1994; Holak, 1980; Greulach and Henze, 1995; Li and Smart, 1996. Equiarte *et al.* 1996).

Another technique applied to the speciation of arsenic is coulometric stripping potentiometry using gold micro-electrodes (Jagner *et al.* 1981; Jagner *et al.* 1987; Huliang *et al.* 1987; Huliang *et al.* 1988; Jagner *et al.* 1992; Jagner *et al.* 1994; Jagner and Wang, 1995; Jagner *et al.* 1996; Ratana-ohpas *et al.* 1997).

Arsenic speciation can also be achieved with atomic absorption spectroscopy techniques coupled with hydride generation and using tubes as atomisers. The arsine generated is decomposed, or atomised, in flame heated quartz tubes (Narsito and Agterdenbos, 1987; Michel *et al.* 1992; Hon *et al.* 1986), flame heated quartz tubes (Van Mol *et al.* 1988; Ricci *et al.* 1981; Sturgeon *et al.* 1989) or graphite tubes (Narsito and Agterdenbos, 1987; Willie, 1996). A trapping medium such as Pd (Doidge and Sturman, 1989) can be used in a graphite furnace. The technique results in increased sensitivity by *in situ* accumulation of As on pre-deposited Pd (Doidge and Sturman, 1989; An *et al.* 1992). Moreover, this also allows for the determination of low arsenic concentrations by incorporating arsine production by flow injection (Nielsen and Hansen, 1997; Masscheleyn *et al.* 1991). The trapping of arsenic on pre-deposited Pd has been applied in this work to determine trace arsenic species in leachates and fresh water samples

In water analysis separation of an analyte by ion exchange involves a process by which ions held onto an insoluble solid are exchanged for an analyte in solution that is brought in contact with the solid. Synthetic ion exchange resins are high molecular weight polymers that contain large numbers of an ionic functional group per molecule (Skoog and West, 1985). Ion-exchange resins can concentrate the analyte and separate it from

interferents. Resins suitable for the fractionation of arsenic are anion-exchange resins, which have acidic groups. Published ion exchange methods for the fractionation and concentration of arsenic are few. Early published methods involved arsenic concentration using alumina (Smith, 1953) but these failed to fractionate the element. Chelating resins such as Chelex-100 can adsorb metals ions, e.g. Fe(III), then the modified Chelex-Fe(III) used to fractionate arsenic in water samples. This approach has been developed in this work.

3.1.3 XAD-4 resin and the isolation of natural organic matter (NOM)

Humic substances act as complexing agents for inorganic cations in aqueous environments (Aiken *et al.* 1979). Metal organic complexes play an important role in biogeochemistry of trace metals in natural waters. Amongst the most common trace elements in fresh water systems are iron and aluminum. Iron and aluminum are both strongly bound to humic substances (HS). This work has shown that iron complexed to HS binds strongly to arsenate (see Chapter 4). Therefore, HS-Fe(III) is a potential site for AsO_4^{3-} binding. An objective was to determine how much arsenate was associated with humic-iron complexes by selectively isolating the HS fraction.

Its is possible to isolate metal-organic complexes from natural waters (Mackey, 1982). Methods for natural organic matter (NOM) concentration have included liquid/liquid extraction, freeze drying, reverse osmosis, resins and activated carbon adsorption (Daignault *et al.* 1988). Adsorption techniques using granular activated carbon exhibit low recoveries (Leenheer, 1978). Anion exchange commonly removes large quantities of organic solutes from water, but the recovery of the organic solutes from the resin is usually poor (Malcom and MacCarthy, 1992). The alternative is to use XAD resins to recover dissolved NOM and any arsenic associated with it. XAD resins have been extensively researched and applied to water chemistry, e.g. in the isolation, concentration, and chromatographic separation of humic substances.

XAD resins are a class of non-ionic, macroporous copolymers, which possess large surface areas. XAD resins have greater adsorption capacities and are easier to elute than alumina, silica gel, nylon, and polyamide powder (Aiken *et al*, 1979). The hydrophobic acid fraction (i.e. fulvic and humic acids) and the hydrophobic neutral fraction can be quantitatively recovered from water by these resins (Malcom and MacCarthy, 1992). The binding of many organic molecules to XAD resins involves physical rather than chemical processes (Mackey, 1982).

XAD-4 is one of the resins that have been used to extract hydrophobic organic compounds from natural waters (Aiken *et al.* 1979, Mackey, 1982, Malcom and MacCarthy, 1992, Pietrzyk and Chi-Hung, 1977). It is a hydrophobic cross-linked polystyrene divinylbenzene copolymer (Mackey, 1982); it is not easily wetted and absorbs little water because of its hydrophobic nature. It has a large surface area and therefore has a high adsorption capacity, especially for low molecular weight organic acids (Aiken *et al.* 1979). The properties of XAD-4 resin are given in Table 3.1.

Any trace metals adsorbed by these resins are associated with the natural NOM. In this research, XAD-4 resin was applied to natural water samples to isolate and pre-concentrate the NOM. In doing so, the arsenic fraction associated through iron bound to the NOM was determined.

Table 3.1: Properties of XAD-4 resin

Composition	**Av. Pore diameter (Angstrom)**	**Specific surface area (m^2/g)**	**Specific pore volume (cm^3/g)**	**Solvent uptake (g/g dry resin)**
Styrene divinylbenzene	50	750	0.99	0.99-1.10

3.1.4 Iminodiacetate IDA resins

Adsorption on chelating resins is one of the most convenient methods for separation and preconcentration of metal ions (Yuchi *et al.* 1997). Chelex 100, a chelating cation exchange resin with iminodiacetic acid (IDA) as the functional group has been utilized for trace metal preconcentration in natural waters (Figura and McDuffle, 1977). The adsorption equilibria of trivalent ions (e.g. Al(III) and Fe(III)) on IDA resins have been studied (Yuchi *et al.* 1997, Liberti and Napoli, 1971, Anderegg, 1986).

Selenium speciation in river waters by adsorption onto Fe(III) modified Chelex 100 resin has been investigated by Ferri and Sangiorgio (1996). The method involved preconcentration of Se(IV) from polluted waters with Fe(III)-loaded Chelex 100 resin, allowing for the discrimination of free and bound fractions of Se(IV). Therefore, due to similar chemical properties of arsenic and selenium oxyanions, this research developed the method for application to arsenic speciation in fresh waters.

3.1.5 Scope of this work

This Chapter reports the development of analytical techniques for the laboratory and *in situ* measurement of arsenic speciation.

Methods developed for arsenic species measurements were appropriate for the systems that were studied in this research. The systems which required arsenic speciation studies were:

i) Leachates derived from mine waste rocks (ppm range).
ii) Freshwater samples (ppb range).
iii) Sediment extracts (ppm range).

The selection and development of the appropriate analytical methods for arsenic speciation were governed by the following factors:

i) Selectivity for individual arsenic species.

ii) Freedom from interferents contained in the sample matrix.

iii) The limit of quantitation and the linear concentration range of determination.

iv) Applicability to field measurements.

v) Simplicity and ease of application.

A standard hydride generation atomic absorption spectrometry method was used for arsenic speciation measurements; it is described in section 2.3.4 of Chapter 2. In addition, two other methods developed for arsenic speciation measurements were based on (a) flow injection analysis-spectrophotometry, and (b) fractionation by XAD-4 and iminodiacetate (Chelex-100) resins.

a) A flow injection analysis protocol was developed to measure arsenic species in leachates derived from waste rocks (ppm range). The characteristics of these waste rocks are described in Chapter 5. The flow injection analysis method was based on the published method by Linares *et al* (1986), but was modified to enhance the sensitivity for arsenate determination.

b) Fresh water samples were collected and the arsenic species fractionated on site using techniques based on separation by XAD-4 and Chelex 100 resins (ppb range). Following field fractionation, the samples were preserved, stored and later measured for fractionated arsenic by hydride generation atomic absorption spectrophotometry. The results from field applications using the resins are given in Chapter 4.

3.2 EXPERIMENTAL

The reagents for the arsenic fractionation methods by Chelex-Fe(III) and XAD-4 resins are described below. The optimised experimental procedures for the molybdenum blue method for the determination of arsenic by FIA spectrometry is described in 2.3.11. Further development of these methods is described in this chapter.

3.2.1 Chelex-Fe(III) fractionation

3.2.1.1 Materials

The resin Chelex 100, a 1% cross-linked polystyrene polymer (50-100 dry mesh) in the sodium form (Sigma) was used in this work. A Sigma data sheet indicated that the minimum ion exchange capacity of the wet resin was 0.4 meq/mL.

3.2.1.2 Reagents

i) 0.01, 0.1, 1.0 M HCl, and NaOH (BDH-Analar) eluants were prepared. The 0.1 M NaOH solution was confirmed (HG-GFAAS) to contain no measurable As(V) or As(III).

ii) A 250 mL solution of 1.0 mM tartaric acid/1.0 mM Fe(III) was prepared by weighing 0.038 g of tartaric acid (BDH-Analar), adding 37.5 mL of 200 ppm Fe(III) and making up to 250 mL. An appropriate amount of HCl (BDH-Analar) was added into the flask (to maintain a pH of 2.8) prior to addition of the Fe(III) and tartaric acid. This solution was stored overnight to allow for equilibration.

iii) The Chelex-Fe(III) resin was prepared in a glass column by passing the equilibrated Fe(III) tartrate solution from (ii) over 5 mL of Chelex 100 resin at ~1 mL/min.

3.2.2 XAD-4 fractionation

The XAD-4 resin available for this work had been pre-cleaned by solvent extraction, as described by Gregor and Powell (1986).

3.2.2.1 Reagents

i) Fulvic acid solutions (17 ppm) were prepared from a 170 ppm standard fulvic acid solution (sample FA4; Gregor *et al.*, 1989) to investigate arsenate and arsenite interactions.

ii) A 0.1 M NaOH eluant solution was prepared from NaOH (BDH-Analar).

iii) A 0.1 M HCl eluant solution was prepared by dilution of conc. HCl (BDH-Aristar).

3.3 RESULTS AND DISCUSSION

3.3.1 Arsenic speciation measurements by FIA with spectrophotometry

The method described in section 2.3.11 was developed from that published by Linares *et al.* (1986). This involved formation of the molybdenum blue complex, $H_3[AsMo_{12}O_{40}]$ and spectrometric detection at 820 nm. Modifications were made to the published method, to increase the sensitivity. These modifications and their experimental validation are described below. The manifold shown in Figure 2.2 was used throughout this work. Reagents are described in section 2.3.11.

3.3.1.1 Modifications applied to the published method

The sensitivity of the method was increased by the following changes:

i) Increasing the molybdate concentration from 0.024 M to 0.12 M.

ii) Inclusion of the catalyst, antimony potassium tartrate ($KSbO.C_4H_4O_6$) in a mixture with the molybdate solution, to enhance the rate of formation of the molybdenum blue complex.

iii) Increasing the reaction temperature from 55 °C to 60 °C.

iv) Increasing the sample loop volume from 150 µL to 240 µL. This volume was later decreased either to 100 or 50 µL for analyses of leachates from the acidic sandstone (which contained high concentrations of arsenic).

Standard 10 µM arsenate solutions were used to monitor the effect on absorbance due to changes applied to the experimental parameters. The results of this investigation are summarised in Table 3.2.

Table 3.2: The effect on heteropolyacid product yield from a 10 μM arsenate solution consequent on changes in reagents and modification to the published FIA manifold. Product concentration determined at λ_{max} (820nm)

Parameter	Absorbance^{+}
MoO_4^{2-} (0.024 M)*	0.06 ± 0.03
MoO_4^{2-} (0.12 M)	0.10 ± 0.02
Sample loop (150 μL)*/0.12 M MoO_4^{2-}	0.10 ± 0.02
Sample loop (240 μL)/ 0.12 M MoO_4^{2-}	0.13 ± 0.02
Water bath temperature (50 °C)*/0.12 M MoO_4^{2-}/240 μL	0.13 ± 0.02
Water bath temperature (60 °C)/ 0.12 M MoO_4^{2-}/240 μL	0.19 ± 0.01
Antimony catalyst/ 0.12 M MoO_4^{2-}/240 μL/60 °C	0.83 ± 0.01

(*) indicates conditions used in the published method by Linares *et al.* (1986). $^{+}$Absorbance (n=5) is expressed as the mean (± SD) for 10 μM arsenate solutions.

As indicated in Table 3.2, modifications of the specified parameters resulted in greater sensitivity for the detection of the arsenate species. The most pronounced increase in absorbance was achieved by inclusion of the antimony catalyst. The antimony catalyst was also utilised in the detection of arsenite species (following their oxidation to arsenate with iodate in the FIA manifold). The detection limit of this method was 0.33 μM ($3\sigma_{blank}$, n=10). The measurements were reproducible, indicative by the small errors in the measurements. The sample throughput was 10-15 samples per hour.

3.3.1.2 Interferences

Samples typically contained ppm levels of calcium and iron. Therefore, the method was checked for possible interferences from these elements by measuring solutions of 5 μM arsenate and 5 μM arsenite in the presence of 600 ppm calcium and 50 ppm Fe. Results indicated that calcium and Fe did not interfere in the formation of the molybdenum blue product.

Investigations were made to determine the effect of acidity (0.001-0.1 M sulfuric acid) on the formation of the molybdenum blue product. The standard method utilises arsenate standards at pH 4. The pH of leachate derived from the sandstone waste rock was 2.9. There was no effect on the molybdenum blue product at this pH, however a decrease of pH to below 2.0 resulted in decreased product formation. This method was applicable to measurement of leachates.

3.3.2 Column fractionation methods using XAD-4 and Chelex-Fe(III) resins

A field method applicable to arsenic speciation in fresh waters was developed using a combination of XAD-4 and the Fe(III) modified Chelex resins. The XAD-4 resin captured arsenate bound to humic-iron/aluminum complexes and the colloidal phase. The Fe(III) modified Chelex resin then captured non-organically bound arsenate (labile arsenate). Arsenic fractionation by these resins was initially conducted on synthetic solutions then later applied to fresh water samples in the field. The procedure involved sequentially passing fresh water samples through the XAD-4 resin and then the Fe(III) modified Chelex resin. The retained fractions were eluted, acidified then stored for arsenic analyses by hydride generation electrothermal atomic absorption spectrophotometry. The final non-retained fraction passing through both resins was also acidified, stored and analysed for arsenic.

3.3.2.1 XAD-4 resin

To determine the amount of arsenic associated with NOM-Fe/Al complexes, equilibrated synthetic solutions containing fulvic acid, Fe(III) and As(V) were passed through an

XAD-4 resin (prior to treatment on the Chelex-Fe(III) resin). Subsequently this method was applied to Devil's Creek samples for on-site fractionation of arsenic (Chapter 4) .

a) Optimised method for arsenic fractionation

Arsenic associated with NOM was fractionated from synthetic and fresh water samples using purified XAD-4. It was established that the most suitable eluting agent was 0.1 M NaOH. For 10 mL of XAD-4 resin the volume of 0.1 M NaOH required for 100 % recovery of arsenic was 20 mL. Initially, quantitative retention and elution of NOM was established with synthetic solutions containing 17 ppm of standard fulvic acid, 500 ppb As(V) and 400 ppb Fe(III). These were prepared by mixing solutions of Fe(III) and fulvic acid to give solutions containing 400 ppb Fe(III) and 17 ppm fulvic acid, then equilibrating for 5 days . This was followed by adding As(V) to give a final concentration of 500 ppb of As(V) and making up to 50 mL, then by further equilibration for 2 days. Samples were fractionated for arsenic according to the following steps:

i) A resin volume of 10 mL was placed in a glass column and pre-washed with 0.1 M HCl (BDH-Aristar).

ii) A 50 mL sample solution (pH 5.0) was passed through the resin at ~1ml/min, then the column was washed with 0.1 M HCl (BDH-Aristar).

iii) Retained NOM and associated arsenic was eluted, firstly with 20 mL of 0.1 M NaOH then with 20 mL of 0.1 M HCl (BDH-Aristar). The eluted base/acid fractions were combined, made up to 50 mL with Milli-Q water and measured for arsenic.

The purpose of the NaOH eluent , was to remove the NOM off the XAD-4 resin through ionisation of the NOM. However, preliminary investigations found that the alkali hydrolysed some Fe(III) bound to NOM to form $Fe(OH)_3$, thereby trapping any arsenate by adsorption. To counter this problem, and recover As trapped by the amorphous $Fe(OH)_3$, acid was used as the final eluant.

b) Arsenic fractionation by XAD-4 resin

The results are shown in Table 3.3.

Table 3.3: Fractions of fulvate bound arsenic retained by and recovered from the XAD-4 resin

Solution#	As species retained by XAD-4 (μg/mL)	% Recovery
As(III)	<DL*	0
As(V)	<DL	0
As(III) + FA**	<DL	0
As(V) + FA	21	4
As(III) + FA + Fe(III)	<DL	0
As(V) + FA + Fe(III)	450 ± 2	90

* <DL is below detection limit of 0.008 ppb. #The concentrations of As(III), As(V) and Fe(III) were 500 ppb. ** Fulvic acid (FA) was 17 ppm. Errors are within 0-10% RSD.

For standard fulvic acid solutions, at a concentration similar to NOM in fresh waters (17 ppm), the fulvic acid was quantitatively retained by and eluted from the resin. This was confirmed by measurement of fulvic acid absorbance at 350 nm. In contrast, the XAD-4 resin did not retain As(III) or As(V) from standard solutions (i.e. containing no ligands). Further, when As(III) and As(V) were added to fulvic acid solutions, only 4% of the As(V) was captured on the resin. This was most likely through adsorption to residual metals attached to the fulvic acid. When As(III) and As(V) were added to fulvic acid equilibrated with Fe(III), no measurable As(III) was retained, whereas the resin retained 90% of As(V). This indicates that the arsenic(V) is coordinated to Fe(III) that is bound to the fulvic acid.

c) Interaction of arsenate with Fe(III) complexed to fulvic acid

It could be inferred from the result for As(V) + FA + Fe(III) that recovery of As(V) on the XAD resin is not quantitative. However the retention of As(V) (90%) is probably

limited by the amount of Fe(III) bound to fulvic acid. Table 3.4 represents the results of experiments in which varying amounts of Fe(III) were added to a fulvic acid solution (17 ppm) in separate 50 mL flasks to give final Fe(III) concentrations of 0-500 ppb. These solutions were equilibrated for 5 days, membrane filtered, and then As(V) was added to give a final concentration of 500 ppb. After final equilibration the solutions were passed through a column containing XAD-4 resin.

Table 3.4: The interaction of As(V) (arsenate) with Fe(III) bound to fulvic acid.

Total Fe(III)-μmoles	Bound Fe(III)-μmoles	Adsorbed arsenate-μmoles
0	0.015	0.014
0.09	0.07	0.072
0.18	0.13	0.12
0.36	0.28	0.29
0.45	0.29	0.30

The ratio of (μmoles Fe bound to fulvic acid)/(total μmoles Fe) is < 1.0 and for the 400 ppb (0.358 μmoles) Fe solution is ca. 0.78. The ratio of (μmoles adsorbed As(V))/(μmoles bound Fe) indicates quantitative retention of arsenate by Fe(III) bound to fulvic acid. It can be inferred from the results in Table 3.4 that arsenate forms a 1:1 complex with Fe(III) bound to fulvic acid. Without added Fe(III), the arsenate interacts only with residual Fe pre-existing on the fulvic acid (row 1 in Table 3.4).

3.3.2.2 Iminodiacetate resin (Chelex-Fe(III))

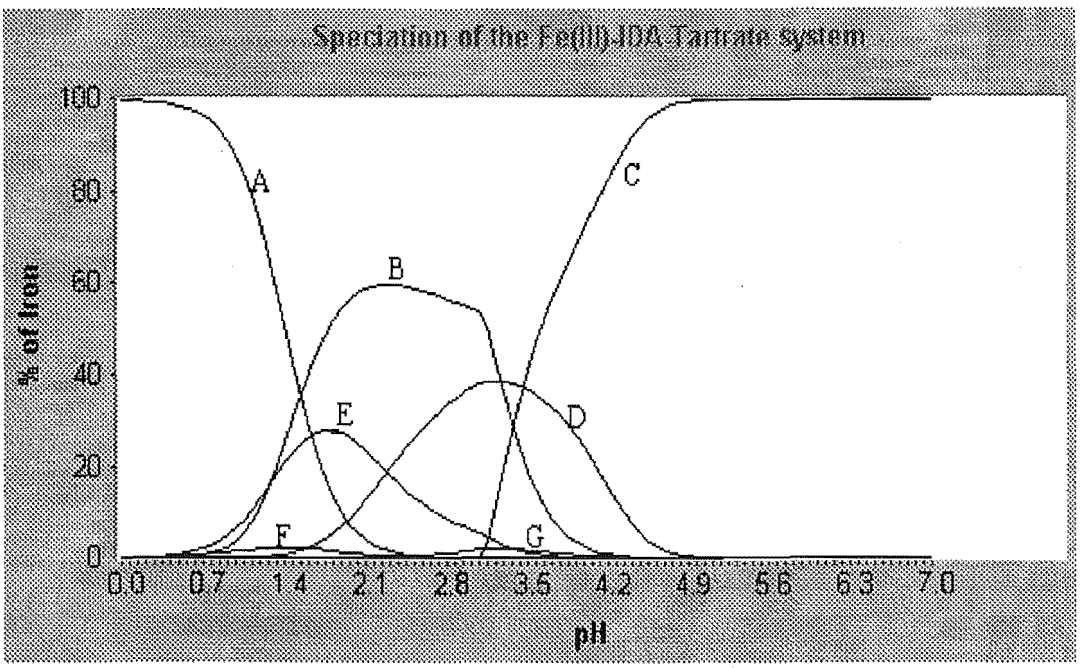
a) Preparation of the resin

Methods were based on the work by Ferri and Sangiorgio (1996) for the determination of selenium in fresh waters. The method involved use of Chelex-Fe(III) resin prepared at 70-80 °C. However this method was found unsuitable for the separation of soluble arsenic species because arsenite was oxidized on passage through the Chelex-Fe(III) resin. The oxidation was most likely due to interaction with entrapped amorphous

$Fe(OH)_3$, a consequence of the method of resin preparation. Therefore, the method of Chelex-Fe(III) resin preparation was modified.

Calculations were made with the 'SPECIES' program (Pettit and Powell, 1999) to determine the optimum pH conditions and reactant concentrations for the formation of Chelex-Fe(III) complexes. The speciation curve is for the formation of Fe(III)-IDA shown in Figure 3.1 and the stability constants for this calculation are shown in Table 8.5. The stability constants was taken from the IUPAC Stability Constants Database (Pettit and Powell, 1997). The calculation was for a solution containing Fe^{3+} (1.0 mmol), IDA (1.0 mmol) and tartrate (1.0 mmol).

Figure 3.1: Species distribution diagram for the binding of IDA and Fe(III).



A is Fe^{3+}, B is Fe(III)-IDA, C is $Fe(OH)_3(s)$, D is $Fe(III)(tartrate)_2$, E is Fe(III)-tartrate, F is $Fe(OH)^{2+}$ and G is Fe(IDA)(OH).

Table 3.5: The stability constants for a Fe(III)-IDA-tartrate system:

$$pFe^{3+} + qH^{+} + rIDA + startrate = Fe_p H_q (IDA)_r (tartrate)_s$$

Reactants	Log $\beta_{p,q,r,s}$	p	q	r	s
IDA-H^+	9.27	0	1	1	0
	11.85	0	2	1	0
	13.75	0	3	1	0
IDA-Fe^{3+}	12.5	1	0	1	0
	12.02	1	1	1	0
	8.01	1	-1	1	0
Fe^{3+} hydrolysis	-2.73	1	-1	0	0
	-3.20	2	-2	0	0
	-6.92	3	-4	0	0
	-5.67	1	-2	0	0
Tartrate	3.93	0	1	0	1
protonation	6.72	0	2	0	1
Tartrate-Fe^{3+}	6.66	1	0	0	1
	12.3	1	0	0	2

To avoid hydrolysis of iron on the resin during the preparation of Chelex-Fe(III), the Fe(III) solution was initially prepared as an Fe(III)-tartrate complex by reaction of 1.0 mmol/L tartaric acid and 1.0 mmol/L Fe(III) at pH 2.8 then allowing the solution to equilibrate overnight. The formation of the Chelex-Fe(III) complex was achieved by passing 250 mL of the Fe(III)-tartrate solution through 5 mL of IDA resin in a glass column.

The 250 mL of Fe(III)-tartrate solution contained 7.5 mg of Fe(III). Analysis of the eluate showed that 98% (7.35 mg) of the Fe(III) was bound onto the Chelex resin. This was approximately 0.1 meq/mL, which did not exceed the maximum wet capacity of the resin.

b) As(III) and As(V)

Initial experiments were undertaken to investigate the retention of arsenic species by the Chelex-Fe(III) resin. The retention was determined by passing standard As(III) and As(V) solutions (pH 4.7) through the column. The solution which passed through the column was analysed for As(III) and As(V) by hydride generation AAS and the columns were also eluted with 0.1 M NaOH (see section e) and the eluant analysed in the same way.

Quantitative retention of As(V) on the Chelex-Fe(III) resin was achieved but As(III) was not retained, as shown Table 3.6. Importantly, there was no oxidation of As(III) to As(V) which would have occurred if $Fe(OH)_3(s)$ was present in the resin.

Table 3.6: Retention of arsenic species on the Chelex-Fe(III) resin.

Solution	Retained (μg/L)	Not retained (μg/L)	% Recovery
400 μg/L As(III)	<DL*	399	0
400 μg/L As(V)	400	<DL*	100

<DL*is below the detection limit of 0.008 μg/L (3σ of the blank, n=3). Errors are within 0-10% RSD.

The principle of fractionation of soluble As(III) and As(V) was established by these experiments. Analyses of duplicate samples established that retention and elution of As(V) was also quantitative at lower concentrations (5, 10 and 20 ppb). The lower concentration of arsenate fractionated by this method is critical because the WHO limit for total arsenic in drinking water is 10 ppb (Edwards, 1994). The results from Devils Creek water samples are given in Chapter 4.

c) Eluant optimisation

Investigations were conducted to determine whether an acid or base was more suitable for eluting As(V) off the column. These studies were done using 50 mL standard solutions of 400 ppb arsenate (pH 4.7) to load 5 mL of Chelex-Fe(III) resin. Both HCl

and NaOH were studied as eluents (Table 3.7) by passing 20 mL of each solution through 5 mL of Chelex-Fe(III) resin (As(V) loaded).

Table 3.7: Investigation of eluents for removal of As(V) from Chelex-Fe(III) resin. The resin was loaded with As(V) from 50 mL of 400 ppb arsenate solution.

Eluant	Arsenate (% Recovery)
0.01 M HCl	<DL*
0.1 M HCl	<DL*
1.0 M HCl	<DL*
0.01 M NaOH	$65 \pm 4^{+}$
0.1 M NaOH	$100 \pm 2^{+}$
1.0 M NaOH	$86 \pm 3^{+}$

* is below detection limit of 0.008 μg/L and $^{+}$ is the standard deviation from the mean (n=3). Errors are within 0-10% RSD.

Retained As(V) was quantitatively eluted from the Chelex-Fe(III) resin with 0.1 M NaOH but was not eluted with HCl. It is assumed that NaOH was effective by virtue of the substitution reaction:

$$Res\text{-}Fe\text{-}OAsO_3H^{+} + OH^{-} = Res\text{-}Fe\text{-}(OH)^{2+} + HAsO_4^{2-} \qquad (3.1)$$

The published method of Ferri and Sangiorgio (1996) used 1 M NaOH as the eluant, however in these investigations it was found unsuitable. It appeared that Fe(III) attached to the IDA resin underwent hydrolysis at the high NaOH concentration. This led to the formation of amorphous $Fe(OH)_3$, which adsorbed and trapped arsenate in the column and promoted oxidation of As(III).

d) Procedure for arsenic fractionation

With this resin preparation, the fractionation of arsenite and arsenate in synthetic and fresh water samples was made possible according to the following steps:

i) The Chelex-Fe(III) resin was pre-washed with dilute HCl (0.001 M) and buffered with dilute acetate buffer (pH 4.7). The dilute buffer was to ensure that pH changes did not occur on passage of sample solution through the Chelex-Fe(III) resin.

ii) Then a water sample (50 mL) was passed through the Chelex-Fe(III) resin at ~1mL/min, and the resin eluted with 20 mL of 0.1M NaOH.

iii) The NaOH eluted fraction was neutralized with HCl (BDH-Aristar) then analysed for arsenic.

iv) KIO_3 was added to the non-retained fraction from (ii).

v) The KIO_3-treated fraction was then passed through the chelex-Fe(III) column. This allowed for the preconcentration of As(III) as oxidised As(V) on resin.

After fractionation of arsenate from the sample (step (ii)), As(III) was pre-oxidized to As(V) (step (iv)) before its concentration on the Chelex-Fe(III) resin (step (v)). As(III) oxidation was conducted with 0.01 M KIO_3 in acidic conditions and was instantaneous at pH 1.0-5.0. The pre-oxidized As(V) was quantitatively retained by the Chelex-Fe(III) resin in the presence of 0.01 M KIO_3.

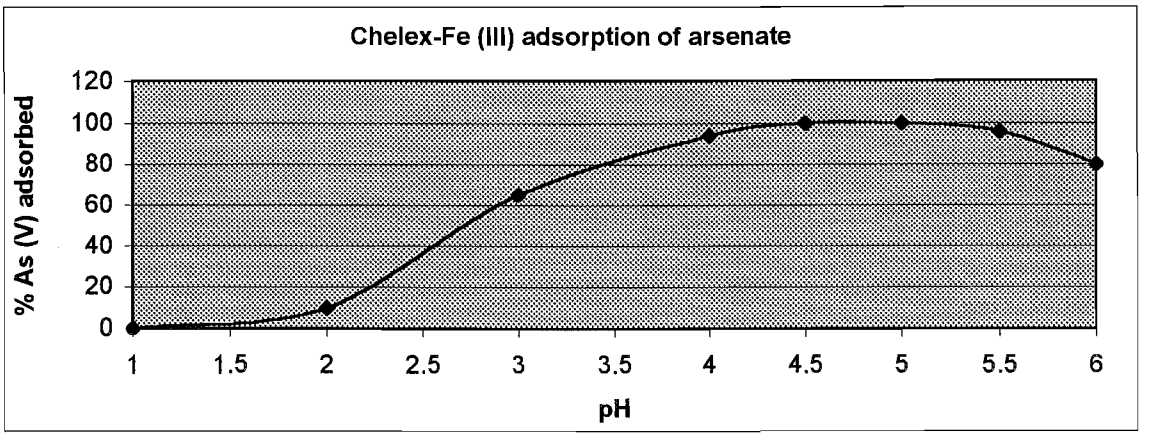
The resin was regenerated after accomplishing the fractionation of 6 samples.

e) Arsenic fractionation by Chelex-Fe(III) as a function of solution pH

Figure 3.2 shows the retention of arsenate as a function of solution pH. The resin adsorbs arsenate, quantitatively in the pH range 4.5 –5.5. Since the dominant arsenate species at this pH is $H_2AsO_4^-$, the association of the resin and $H_2AsO_4^-$ can be represented by the following equation:

$$Res\text{-}Fe(OH)^{2+} + H_2AsO_4^- = Res\text{-}Fe\text{-}OAsO_3H^+ + H_2O \qquad (3.2)$$

Figure 3.2: The retention of As(V) from 50 mL solutions of 400 ppb As(V), on Chelex-Fe(III) resin (5mL) as a function of solution pH. The column is initially buffered at pH 4.7.



3.4 SUMMARY

The FIA method for As fractionation is laboratory based, is cheap and non-high tech but has a relatively high DL and is labour intensive. The hydride generation AAS method (section 2.3.4) was the preferred method of analysis in this work. The method is advantageous due to its ease and simplicity and it is a very sensitive method (DL = 0.008 ppb) therefore making it applicable to determination of arsenic at the trace level. Field work using Chelex-Fe(III) and XAD-4 resins for the fractionation of arsenic species also utilised the hydride generation AAS for arsenic measurements because the arsenic fractionated was at the ppb level. The XAD-4 and Chelex-Fe(III) method is simple and convenient for on site As fractionation and is the preferred method when there is a long delay time between field work and analysis in the laboratory.

CHAPTER 4

CHARACTERISATION OF CATCHMENT AREA: WATER AND SEDIMENT ANALYSES

This chapter discusses the distribution of arsenic in fresh waters and sediments. It reports the characterisation of water and sediment samples from the Devils Creek catchment. The location of the Devils Creek catchment area is given in Figure 1.2. Old mine workings are located in the upper reaches of both Devils and Oriental Creeks, above sampling points 1 and 2.

Part I: CHARACTERISATION OF DEVILS CREEK WATER SAMPLES

4.1 INTRODUCTION

Fresh waters, such as in the Devils Creek catchment, are complex heterogeneous electrolyte systems containing both inorganic and organic matter. The systems therefore can not be fully defined (Eichenberger and Chen, 1982). The freshwater chemistry is even more complex when considering the interaction of numerous inorganic or organic ions with arsenic.

Sources of pollutants in fresh water streams are either natural (through the weathering of minerals) or anthropogenic (e.g. through mining activity). In many areas where there have been disruptions of natural materials through mining, the exposed material can

weather at accelerated rates. Such is the case of acid mine drainage (Eichenberger and Chen, 1982) which is discussed in Chapter 1.

Trace arsenic is present in fresh water in two physical forms: as dissolved species or associated with solid particles. Due to physical, chemical and biological reactions within the water, there may be dynamic processes linking the various particle-adsorbed species and soluble species. The aqueous phase contains both free and complexed species. In the solid form, whether in deposited sediments or in suspended particulate matter, arsenic can be complexed to clays, organic matter, Fe or Mn oxides, carbonates and sulfides, or associated with microorganisms (Bourg, 1988; Fergusson, 1990).

The distribution of arsenic between suspended sediments and freshwaters will depend on a number of factors, of which the most important are the speciation in solution and environmental variables. The environmental variables with the greatest influence are pH, E_h (aerobic or anaerobic nature of the water), concentration of the arsenic species, the type and amount of NOM present, and the type and amount of colloidal and particulate matter (Hart and Davies, 1978; Eichenberger and Chen, 1982; Bourg, 1988). Elements such as Fe, with its Fe(II)/Fe(III) redox couple, are predominant participants in aquatic redox processes (Stumm and Morgan, 1996). Moreover, the Fe redox state may affect the distribution of arsenic between suspended sediments and the water column. This is through the formation of insoluble colloidal complexes such as those with iron(III) hydroxides. Under reducing conditions conversion of Fe(III) to Fe(II) will release arsenic from sediments (Ferguson and Gavis, 1972). The sediment-water interface is where the concentration of iron rich precipitates is greatest.

Changing redox environments can also affect the arsenic concentration in freshwaters by direct changes in the oxidation state of arsenic and by redox changes in the ligands such as NOM that compete for binding sites on iron hydroxides (Hart and Davies, 1978; Rubin, 1976; Eichenberger and Chen, 1982; Fergusson, 1990). Fluxes of arsenic across the solid-water interface occur in response to the changing environmental conditions as the system progresses towards equilibrium. An increase in the dissolved arsenic will be

compensated for by adsorption or precipitation. Conversely, a decrease in dissolved arsenic can enable remobilisation (Bourg, 1988).

NOM is able to react with metal ions such as iron(III). The resultant NOM-Fe(III) compounds can complex arsenic via the Fe(III) centre. Other anions are likely to compete in this process, e.g. sulfate (Rubin, 1976; Eichenberger and Chen, 1982).

It was considered important to study the speciation and the distribution of arsenic between the water column and natural sediments in Devils Creek to gain an appreciation of concentrations and variability at this stage before the mine has commenced operations.

4.2 SCOPE OF THIS WORK

The Devils Creek catchment study was partially concerned with establishing the existing baseline levels of arsenic in the fresh water. Of interest were constituents such as arsenic, iron and sulfate, which would be directly affected by mine derived leachates. The objectives of this study were to establish for the water column:

i) baseline levels of arsenic; the extent to which arsenic is transported downstream;
ii) the speciation of arsenic;
iii) baseline levels of major elements, pH, sulfate and NOM.

The objectives were achieved by:

i) measurement of arsenic at several sites downstream of the proposed mine site
ii) fractionation of arsenic on-site.
iii) laboratory analysis of samples for iron, arsenic, sulfate, NOM, pH and major elements.

4.3 EXPERIMENTAL

Devils Creek water samples were collected in August 1999 from five sites whose locations are described in section 2.3.12(a) and in Figure 1.3. The fractionation of arsenic was done by sequentially passing samples through columns containing XAD-4 and the modified Chelex-Fe(III) resins. This fractionation was effected in the field immediately following sample collection; column eluates were then stored prior to laboratory measurements for arsenic using HG-GFAAS. The total arsenic was also measured in separate samples collected from the same sites. The methods describing the resin preparation, the development work on these resins and measurement of arsenic by HG-GFAAS are described in Chapter 3. The preservation and storage of fresh water samples is described in Chapter 2. The instrumental methods used for measurement of the pH, sulfate, NOM, Fe (by GFAAS) and the ICP analysis of water samples are given in Chapter 2.

Colloidal Fe and arsenic were determined by passing 1 L of water samples through 0.025 μm membrane filters. The filtered residue was dissolved with 0.1 M HCl (Aristar-BDH), making up to 25 mL and analysing for Fe and arsenic as described in Chapter 2.

4.4 RESULTS AND DISCUSSION

4.4.1 General parameters

The temperature and pH were measured on the day of sampling. These results are shown in Table 4.1 together with those for NOM and sulfate. The concentration of NOM in Devils Creek ranged from 10-13 mg/L. NOM arises as a refractory end product from the degradation of plant debris in soils, and is leached from soil into the waterways. An acidic pH is normally expected for any stream containing organic matter. However, the near neutral pH values (6.5-7.1) measured in the stream indicate that the pH is controlled

by the basic rocks in the catchment. Sulfate is the product of oxidation and leaching of pyrite containing minerals; such leachates drain into Devils Creek from the catchment.

Table 4.1: The temperature, pH, NOM and sulfate concentration in Devils Creek water samples.

Sample Site	Temperature (°C)	pH	NOM (μg/mL)	Sulfate (μg/mL)
S1	4	6.5	13	26
S2	4	6.8	12	11
S3	5	7	11	23
S4	5	7.1	10	20
S5	5	7.1	11	20

The major elements quantified in the Devils Creek water samples by ICP-AES were Ca, Fe, K, Mg, Mn, Na and S (Table 4.2). Other elements also detected but with concentrations below the limit of quantitation were Al, Cd, Cr, Cu, Mo, P and Zn. Where the concentrations are higher in the non-filtered samples than in filtered samples this indicates that some of the elements exist in the colloidal form. This is particularly noted for both Fe and Mn, which have a strong tendency to form colloidal oxides. The ratio of calcium to magnesium was low (Ca/Mg; ~1.1). This may indicate weathering of both limestone and dolomite ($CaMg(CO_3)_2$) which has an Ca/Mg ratio of 1.7. This process could contribute to the high pH of the stream.

Compounds existing in the colloidal form exist at particle size > 0.025μm (Fergusson, 1990) and are removed by the 0.025μm membrane filters.

Table 4.2: The major elements in the Devils Creek water samples as measured by ICP-AES

Sample Site	Filtration*	Ca	Fe	K	Mg	Mn	Na	S
S1	Unfiltered	5.6	0.26	0.46	4.8	0.012	5.8	6.2
S1	Filtered	7.5	0.26	0.72	6.6	0.007	7.1	8.3
S2	Unfiltered	4.4	0.29	<0.1	5.4	<0.0002	4.9	1.5
S2	Filtered	3.7	0.18	<0.11	4.6	<0.0002	3.3	1.4
S3	Unfiltered	6.9	0.32	0.71	6.4	0.012	6.6	6.7
S3	Filtered	6.6	0.21	0.53	6.0	<0.0002	6.7	6.4
S4	Unfiltered	7.1	0.31	0.75	6.5	0.014	7.1	6.1
S4	Filtered	4.9	0.09	0.53	4.5	0.002	5.1	4.4
S5	Unfiltered	5.4	0.25	0.61	4.9	0.024	8.3	4.2
S5	Filtered	5.7	0.12	0.63	5.3	0.003	6.0	4.5

Concentrations expressed as *μg/mL*. *Filtered samples refer to samples filtered using 0.025μm membrane filters.

4.4.2 Total and fractionated arsenic

The results for As(III), As(V), organically bound arsenic and total arsenic are shown in Table 4.3. Table 4.4 shows the concentrations of colloidal Fe and As(V) in the Devils Creek water.

Table 4.3: Arsenic fractions in the Devils Creek water samples

Sample site	As(III) (μg/L)			As(V) (μg/L)		
	Chelex *a*	XAD *b*	HG *c*	Chelex *a*	XAD *b*	HG *c*
S1	<DL	<DL	10	113	30	144
S2	<DL	<DL	9	76	21	96
S3	<DL	<DL	<DL	112	28	142
S4	<DL	<DL	<DL	109	22	145
S5	<DL	<DL	<DL	114	15	136

The DL is 0.008 μg/L (3σ of the blank); (*a*) is the fraction retained by the Chelex-Fe (III) resin; (*b*) is the fraction retained by the XAD-4 resin and (*c*) is the total arsenic of the oxidation state indicated (0.025 μm membrane filtered samples) determined by HG-GFAAS. Errors are within 0-10% RSD.

Table 4.4: The concentration of colloidal Fe and As(V) in Devils Creek water samples. The As(V) was measured using speciation via HG-GFAAS measurements which detected no As(III) in the dissolved colloids.

Sample site	Fe	As(V)
S1	28	5
S2	33	9
S3	22	6
S4	29	4
S5	18	5

The concentration of colloidal Fe and As(V) are expressed as μg/L. Errors are within 0-10% RSD.

The As(III) fraction was not captured by either resin (samples 1 and 2). This implies that As(III) is not bound to the NOM, or to the Fe(III) modified Chelex resin. As described in Chapter 3, As(V) will bind to Fe(III) attached to NOM or attached to the Chelex resin.

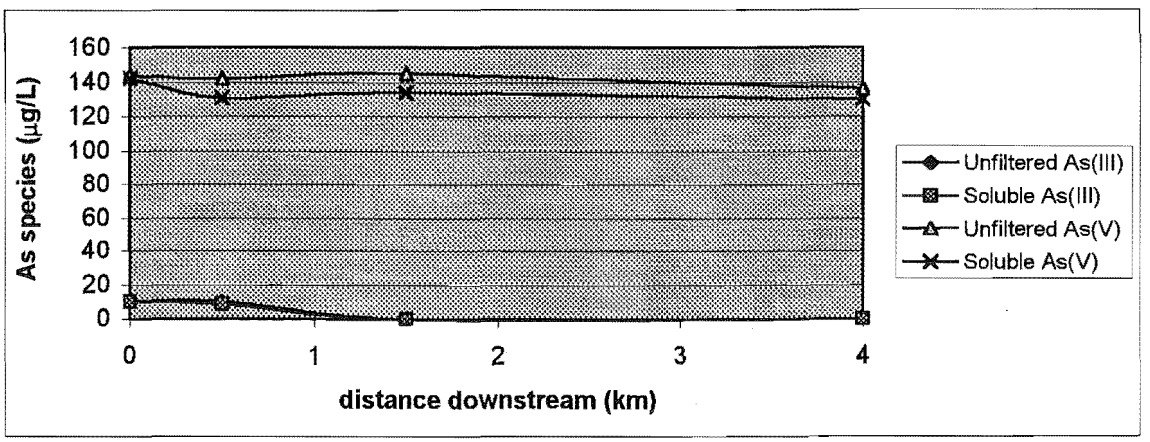
As(V) fractions were captured by both the XAD-4 and the Chelex-Fe(III) resins. Retention by the XAD-4 resin implies that some As(V) is bound to Fe(III) complexed to NOM and/or Fe(III)-hydroxy colloids (Table 4.4). It is well known that As(V) is strongly adsorbed to Fe(III) hydroxy colloids (Moore and Pierce, 1982; Hering and Wilkie, 1996; Hering *et al.* 1996; Hering *et al.* 1997). In field sampling these colloids were captured by the XAD-4 resin because the water samples were not membrane filtered prior to fractionation. During development work for the XAD-4 resin method it was established that arsenate and Fe(III) interact to form a 1:1 complex when arsenate is equilibrated with an Fe(III) substituted fulvic acid. Results for the As(V)-Fe(III)-fulvic acid interactions are given in section 3.3.3.4. Although aluminum is another metal that associates with NOM, this element is not a major component in the Devils Creek water. Therefore, Fe(III) must be responsible for the association of As(V) with NOM. In addition to arsenate associated with the organic fraction, As(V) was also present as non-complexed arsenate; the Chelex-

Fe(III) resin captured this fraction. The results in Table 4.3 indicate that *ca* 70-90% of As(V) is present as non-complexed arsenate.

There is a good agreement between total As determined by HG-GFAAS and the sum of the As(V) determined in the XAD-4 and the Chelex-Fe(III) fraction. However the total arsenic concentration was 25 % lower than concentration reported value for S3 (Macraes Mining Company, 1994). This difference could be attributed to the variation in stream flow, as stream flow is proportional to As concentration in the fresh water stream.

Figure 4.1 plots the data from Table 4.3. It shows the concentration of arsenic species as a function of distance downstream from sites 1 to 5 (see Figure 1.2). The results show that As(III) concentrations are uniformly low and decrease downstream. This change can be ascribed to oxidation to arsenate in the presence of Fe and Mn oxides. The As(V) concentration remains constant. This indicates that arsenate is not captured by sediments. This result is consistent with the observed saturation of sediments with arsenate (section 4.9.2).

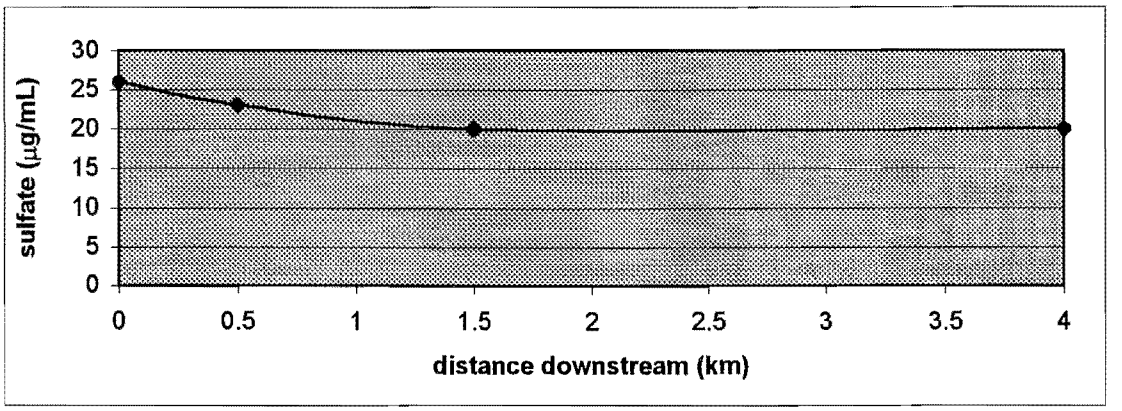
Figure 4.1: Arsenite and arsenate concentrations in Devils Creek.



4.4.3 Sulfate

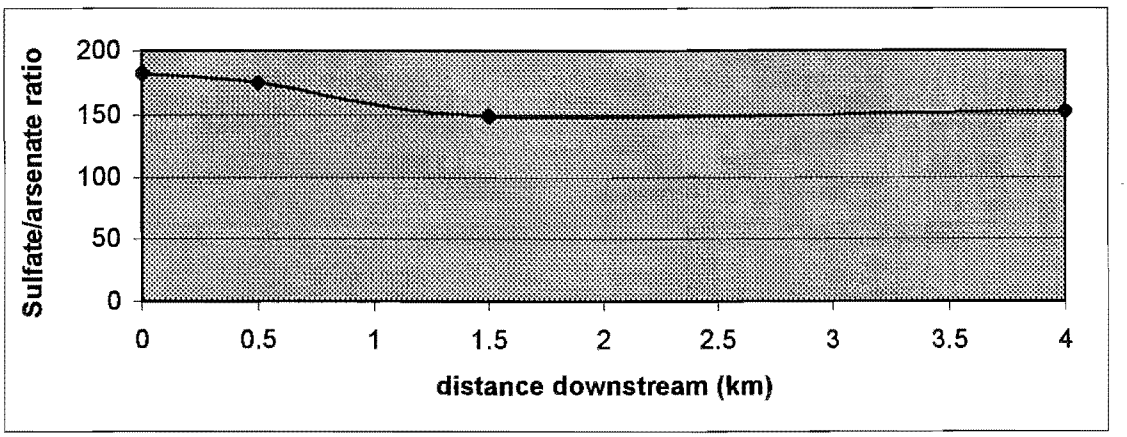
As shown in Figure 4.2, the concentration of sulfate at site 1 was 26 mg/L. However, after the confluence of Oriental Creek (site 3) the concentration is lower by 4 mg/L due to dilution.

Figure 4.2: Sulfate in 0.025 μm membrane filtered water samples from Devils Creek. Data represented are for sites 1, 3, 4 and 5.



Sulfate concentration is an important marker because sulfate is not significantly adsorbed onto iron-rich sediments. The only source of sulfate is from oxidation of natural sulfur rich rocks and old mine workings. Drainage and tributaries downstream are likely to decrease, rather than increase the concentration of sulfate as indicated in Figure 4.2. The ratio (SO_4^{2-}/AsO_4^{3-}) can be used as an indicator of the extent to which As(V) is adsorbed onto stream sediments. From data in Figures 4.1, 4.2 and 4.3 it can be established that the SO_4^{2-}/AsO_4^{3-} ratio decreases slightly in the upper reaches of the Devils Creek, but remains constant at *ca* ~150 (filtered samples) with respect to distance downstream. This indicates that there is little interaction of arsenate with stream sediments.

Figure 4.3: The ratio of sulfate/arsenate in Devils Creek (0.025 μm membrane filtered). Data represented are for sites 1, 3, 4 and 5.



4.5 CONCLUSION

The water in Devils Creek Catchment contains high arsenic. This arises from leaching of waste rocks from old mine workings within the catchment. This could also apply to sulfate. Most of the arsenic is soluble, with As(V) the predominant species. A minor fraction (13-28%) is bound to NOM. The low As(III) concentration is most likely a result of oxidation, facilitated by the high pH of the freshwater and through interaction with suspended and bottom sediments that contain hydrous oxides of manganese and iron. Obviously any future arsenic release from leaching of mine waste rocks would result in increased arsenic in the water column.

Part II: ARSENIC INTERACTION WITH SEDIMENTS

4.6 INTRODUCTION

Sediments in rivers or streams are important materials as they can be the main location, source and carrier of arsenic (Hart and Davies, 1978; Salomons and Forstner, 1984; Fergusson, 1990). Sediments can influence the composition and hence speciation of arsenic in the water column (Hart and Davies, 1978). The transport of sediments is strongly related to hydrological and geo-morphological phenomena. The main processes are:

i) Erosion of sediments from bottom or a bank.

ii) Vertical and horizontal transport of particles in the water

iii) Deposition on the bottom.

iv) Compaction of the deposit.

In flowing streams, sediments will settle when the water flow is below a certain critical velocity (Salomons and Forstner, 1984; Forstner, 1989, Fergusson, 1990). Above this velocity, particles will be transported.

Solid phases can interact with dissolved constituents such as arsenic. The concentration of arsenic in the water column decreases through its association with the solid phase. This arises through physical and chemical processes such as adsorption, ion exchange or coprecipitation. These processes will affect the distribution pattern through the system (Rubin, 1976, Forstner, 1989; Fergusson, 1990; Dzombak and Morel, 1990; Bourg and Loch, 1995). Arsenic (or metals) will not be permanently fixed by the sediments, but can be recycled by biological and chemical agents, both within the sediments and back into the water column (Salomons and Forstner, 1984).

The important parameters that can control the solubility of arsenic in fresh water sediments are pH, E_h, ionic strength the speciation of arsenic, and the concentration of humic substances or competing anions and cations (Rubin, 1976). This is consistent with the observation that the sorption of arsenic on synthetic hydrous oxides is strongly dependent on solution pH, ionic strength, and the presence of competing ions (Dzombak and Morel, 1990). Rubin (1976) noted that water pH can control solubilisation or agglomeration and therefore subsequent sedimentation of the arsenic.

The presence of competing ions can promote desorption or dissociation of arsenate from sediments. This can arise from the competitive binding of NOM, sulfate and calcium, to adsorption or complexing sites. Desorption of arsenic from sediments can also be promoted by change in pH, or arsenic concentration in the interstitial water of sediments. In addition, changes in the sediment phases (calcium carbonate and oxides of iron, manganese and aluminium) will affect the solubility of arsenic (Moore, 1990).

Sediments have been classified in a variety of ways according to criteria such as source, particle size, and composition. The more important size groupings are; sand 63-2000 μm, silt 2-63 μm and clay <2 μm. The major components of the <63 μm fraction include clays, quartz, feldspars, various silicate minerals, gibbsite, calcium carbonate and organic solids. These can be coated with hydrous oxides of Mn and Fe and NOM. These oxides are the prime agents for adsorption of inorganic components (Salomons and Forstner, 1984; Forstner, 1989; Fergusson, 1990; Dzombak and Morel, 1990; Bourg and Loch, 1995).

Analysis of sediments can be achieved through an initial wet sieving and, drying, followed by relevant sample preparation. When the sample is wet sieved using water of the same system the element measurement does not alter (Forstner, 1989). Sieving concentrates the grain fraction containing the substances active in pollutant enrichment, i.e. hydrates, sulfides, amorphous and fine-grained organic materials. The use of 63 μm sieves (Fergusson, 1990) separates these finer fractions of interest. The <63 μm fraction is recommended for the following reasons (Salomons and Forstner, 1984):

i) Trace metals (and therefore arsenic) have been found to be present mainly in association with the clay and silt particles.

ii) This material is also carried in suspension, which contributes to transport.

4.7 SCOPE OF THIS WORK

The premise for this work was that sediments could be used to indicate the quality of the Devils Creek water both before and after anthropogenic activity such as mining development could affect the catchment. By accumulation or release of As, the sediments integrate variable effects over a period of time. This is because oxidising or reducing conditions could result in accumulation (formation of colloidal As compounds and therefore sedimentation) or release respectively.

The objectives of studies with the Devils Creek sediments were concerned with establishing the:

iv) Baseline levels of arsenic in different mineral phases in the sediments.

v) Baseline levels of minor elements in the sediments (Fe, Al, Ca, Cd, Cr, Cu, K, Mg, Mn, Mo, Na, P, S, Zn).

vi) Arsenic complexation capacity of the sediments.

The objectives were achieved by determining the:

i) Arsenic concentration in the <63 μm sediment fraction by applying sequential chemical extractions.

ii) Total concentrations of minor elements using acid digestion.

iii) Arsenic complexation capacity of the sediments by titrating <63 μm sediments with know amounts of arsenate.

4.8 EXPERIMENTAL

Devils Creek sediments were wet sieved to <63 μm and dried. The arsenic concentrations associated with each mineral phase in the sediments were established through chemical extraction as outlined in the procedures in section 2.3.13. The samples for determination of minor elements by ICP-AES were digested according to the procedure also in section 2.3.13.

The capacity of sediments to adsorb arsenic was determined on sediments samples taken from site 3 and 5. This was achieved by titrating <63 μm sediments (1 g) in 200 mL of Milli-Q water with aliquots of As(V) to achieve solution concentrations of 4 –16 ppb for site 3 and 20-200 ppb for site 5. Then the amount of unbound arsenate was determined after an equilibration period of 30 minutes. The solution pH was maintained at 4.7 with a 0.1 M acetate buffer. The pH of 4.7 was chosen to mimic the expected pH of leachate arising from acid mine drainage.

4.9 RESULTS AND DISCUSSION

4.9.1 Major elements and arsenic phases in sediments

Table 4.4 records the analytical results for major and minor element concentrations. The elements with highest concentrations were iron and aluminium. The concentrations ranged from 21,800–34,600 μg/g for iron and 10,900-17,600 μg/g for aluminium. This was a significant result as oxides of these metals (Al oxides to a lesser extent), plus those of manganese, are responsible for the adsorption of arsenate. The other elements, which can interact with arsenic to form insoluble compounds, are calcium and manganese. The concentrations of these were 1,460-2,545 μg/g for calcium and 220-1,625 μg/g for manganese.

Overall for all the elements their concentrations show an increase (e.g. Fe by 59%) with distance downstream. The increase can be attributed to elements being leached from rocks and soils within the Devil's Creek course.

Table 4.5 shows the concentrations of arsenic bound to different mineral phases in Devils Creek sediments. The concentrations were in the following order (for explanation see Table 4.5 footnote); 'iron arsenate' > 'calcium arsenate' > iron occluded > organically bound arsenate> 'aluminium arsenate' > soluble arsenate> loosely bound arsenate. The phase with the greatest amount of bound arsenic is dominated by Fe(III). This clearly indicates that most of the arsenic associated with sediments of Devils Creek is bound mainly to iron phase of the sediment. The quantity of arsenate bound to iron is similar for sediment samples from both the middle and lower stretches of Devils Creek. These results are consistent with the arsenic binding capacity measurements (see section 4.9.2), which indicate that all of the available binding sites in the sediments (i.e. oxides of iron) are saturated with arsenate.

With the exception of the soluble fraction, the accumulation of As(III) in all other sediment fractions was below the detection limit of the HG-GFAAS method. The reason for this is that arsenate interacts much more strongly with the phases in the sediments. Further any As(III) in solution may be oxidised to As(V) by oxides of manganese and iron (Oscarson *et al.* (1980)) and therefore eventually bound to the sediments.

Table 4.4: Major and minor elements determined by ICP-AES on acid digests for <63 μm sediment fractions from the Devils Creek.

Element	Site 1	Site 2	Site 3	Site 4	Site 5
Al	10,900	12,850	17,600	12,500	17,400
Ca	1,740	1,460	2,545	1,765	2,480
Cr	6.5	7.5	9.5	8.5	9.5
Cu	21	31	33	28	31
Fe	24,750	27,750	34,600	21,800	34,050
K	1,135	1,055	1,980	1650	2,190
Mg	3,015	3,400	4,110	3,285	4,185
Mn	1,080	305	1,625	220	1,570
Mo	<DL	<DL	<DL	<DL	<DL
P	635	790	935	685	920
S	190	415	300	710	285
Zn	95	105	140	95	140

Results in Table 4.4 are expressed as μg/g of the sample digest. <DL is less than the limit of quantitation of 0.01 μg/mL for sample digests measured by ICP

Table 4.5: Arsenic fractionation in Devils Creek (<63 μm) sediments. Results expressed as μg As/g of sediments.

Phase		Devils Creek S3 (*μg As/g*)	Devils Creek S5 (*μg As/g*)
F1	*As(III)*	1.52	1.36
	As(V)	2.77	2.73
F2	*As(V)*	1.38	1.42
F3	*As(V)*	4.67	4.62
F4	*As(V)*	5.60	5.35
F5	*As(V)*	105	110
F6	*As(V)*	69	75
F7	*As(V)*	26	24
F8	*As(V)*	5.7	5.2
Total arsenic		355	346

The fractions of arsenic in sediments are; F1 is soluble As (Milli-Q water extraction); F2 is loosely bound As (1.0 M NH_4Cl); F3 is aluminium arsenate (0.5 M NH_4F); F4 is manganese arsenate (0.1 M hydroxylamine hydrochloride and 1.0 M ammonium acetate); F5 is iron arsenate (0.1 M NaOH); F6 is calcium arsenate (0.5 M sulfuric acid); F7 is iron occluded (0.3 M Na-citrate and 0.5 g of $Na_2S_2O_6$ at 90 °C) ; F8 is organic bound arsenate (H_2O_2 at 90 °C then extract residue with 1.2 M NH_4OAc/20%HCl). The specific details for each chemical extraction is given in section 2.3.13.

4.9.2 Arsenic complexation capacity

The complexation capacity measurements were made on <63 μm fractions of sediments sampled from sites 3 and 5 (taken from the middle and lower locations respectively in the Devils Creek catchment). The purpose of these measurements was to determine whether the sediments have the capacity to adsorb further arsenic from the water column. The results are shown as complexation capacity plots in Figures 4.4 and 4.5. The complexation capacity is indicated by the intercept of the line with the abscissa. In summary, the plots show that the sediments did not adsorb added As(V). This implies

that the binding sites in the sediments are saturated with arsenate (and/or other components such as heavy metals). Therefore the sediments are not able adsorb further added arsenic. This result is consistent with the high concentration of arsenate extracted from the mineral phases.

Figure 4.4: The complexation capacity of <63 μm fraction of sediments (pH 4.7 with 0.1 M acetate buffer) for the Devils Creek sediments at sampling site 3.

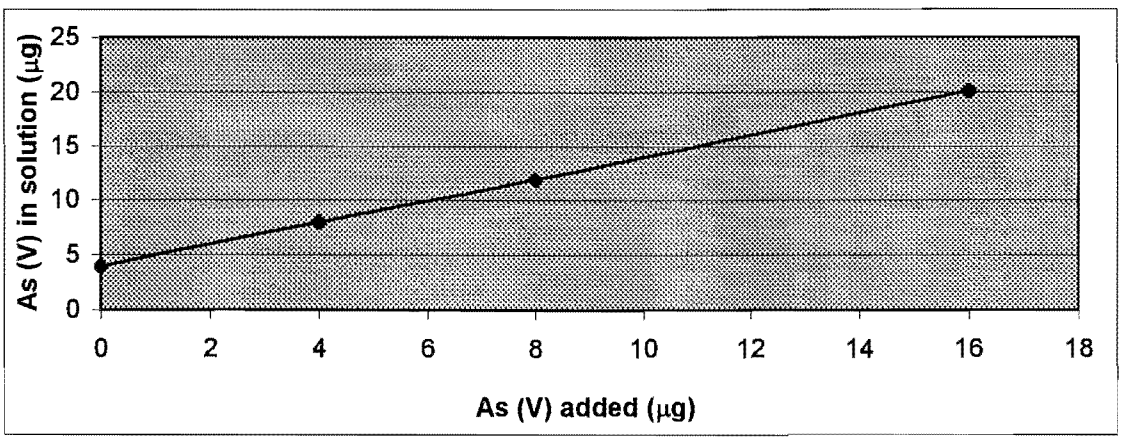
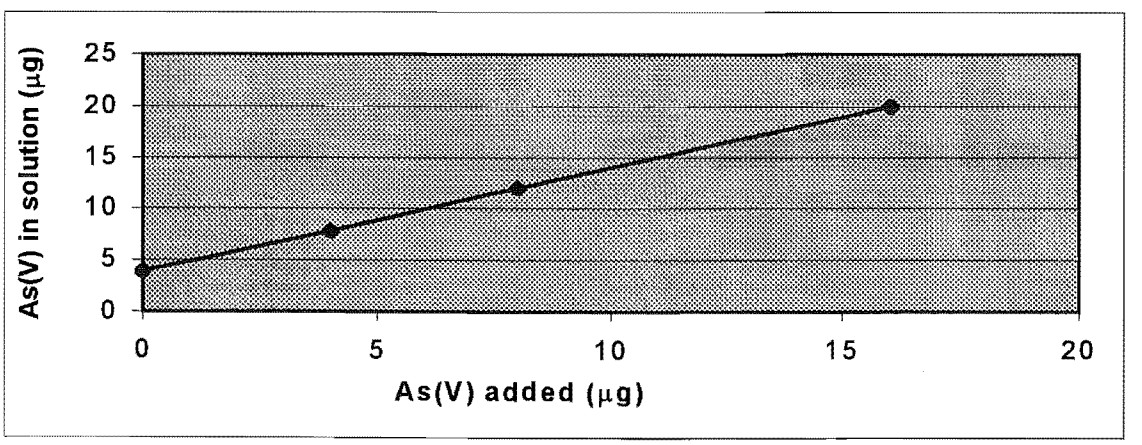


Figure 4.5: The complexation capacity of <63 μm fraction of sediments (pH 4.7 with 0.1 M acetate buffer) for the Devils Creek sediments at sampling site 5.



4.10 CONCLUSION

The major arsenic phases in the Devils Creek sediments are iron, calcium and aluminium arsenates. The high concentration of arsenic in the sediments could arise from the natural geological materials and leaching from old mine workings within the Devils Creek catchment. Due to the high-accumulated arsenic load in the sediments, it is no longer possible for further uptake of arsenic from the water column. This is because potential binding sites in the sediments have been saturated. This is consistent with the results of a constant ratio of sulfate to arsenic down Devils Creek. Therefore, any further arsenic added to the water column (e.g. from mining activities) would be transported downstream without interacting with sediments.

The impact of lowering the pH in the catchment because of AMD is likely to be desorption of arsenic from the sediments into the water column, resulting in increased soluble arsenic. This could also affect the speciation through changes in the redox state of the sediments.

CHAPTER 5

ARSENIC INTERACTIONS WITH AMORPHOUS IRON HYDROXIDES AND HUMIC SUBSTANCES

This Chapter discusses the interaction of arsenic with synthetic amorphous iron hydroxides in the presence of humic substances and competing ions.

5.1 INTRODUCTION

Arsenic adsorption by iron oxyhydroxides (and manganese) is a potential route for regulating the chemistry of the element in fresh waters (Hart and Davies, 1978). Oxyhydroxides are common natural materials that occur as colloidal particles in water. These colloids are stable in solution when the fresh water chemistry does not cause particle flocculation and settling. Under such conditions, colloidal particles remain in suspension. This is because of mutual charge repulsion and Brownian motion. They can therefore be transported by fresh water at its velocity (Stumm and Morgan, 1996, Langmuir, 1997; Thurman, 1985).

The oxyhydroxides and other particulate matter contain ionisable functional groups. They can be –OH (for solid hydroxides, clay minerals and living organic matter), -COOH and $-NH_2$ (organic matter) (Bourg, 1988). In aqueous medium, these surface groups are susceptible to proton transfer, to an extent which depends upon the pH of the solution. For example, the surface sites, ≡S-OH on all hydrous oxides behave amphoterically:

$$\equiv S\text{-}OH_2^+ \longleftrightarrow \equiv S\text{-}OH \longleftrightarrow \equiv S\text{-}O^- \qquad (5.1)$$

Therefore, the net surface charge is positive at low pH and negative at high pH. The pH at which the oxyhydroxide surface has zero net charge is called the point of zero charge (pH_{zpc}). For ferric hydroxides the pH_{zpc} is near pH 8; it also corresponds to the pH of minimum solubility. At pH_{zpc}, there is no ionic repulsion between particles so there is a tendency for them to agglomerate or flocculate (due to van der Waals forces) and settle out (Dzombak and Morel, 1990; Stumm, 1992; Langmuir, 1997).

The adsorption of inorganic anions (e.g. arsenic) and organic anions can be explained by competition with OH^- for surface sites (Rubin, 1976; Eichenberger and Chen, 1982; Dzombak and Morel, 1990; Stumm, 1992).

$$\equiv SOH + A^{z-} \longleftrightarrow \equiv SA^{(z-1)-} + OH^- \quad (5.2)$$

or

$$(\equiv SOH)_2 + A^{z-} \longleftrightarrow (\equiv S)_2A^{(z-2)-} + 2\,OH^- \quad (5.3)$$

For protonated ligands, the ligand exchange can be followed by deprotonation:

$$\equiv SOH + HA^{(z-1)-} \longleftrightarrow \equiv SHA^{(z-2)-} + OH^- \longleftrightarrow \equiv SA^{(z-1)-} + H_2O \quad (5.4)$$

The adsorption of cations can be explained in terms of competition with protons for surface sites, according to the following equations:

$$\equiv SOH + M^{z+} \longleftrightarrow \equiv SOM^{(z-1)+} + H^+ \quad (5.5)$$

or

$$\equiv SOH_2^+ + M^{z+} \longleftrightarrow \equiv SOHM^{(z-1)+} + H^+ \quad (5.6)$$

or

$$(\equiv SOH)_2 + M^{z+} \longleftrightarrow (\equiv SO)_2M^{(z-2)+} + 2\,H^+ \quad (5.7)$$

For the adsorption of each metal the adsorption edge is strongly pH dependent (Bourg, 1988; Dzombak and Morel, 1990; Stumm, 1992).

Adsorption studies for arsenite and arsenate on ferrihydrite (Moore and Pierce, 1982) over the concentration range $10^{-7} - 10^{-3}$ M and pH range 4-10, indicated that adsorption is a function of pH. It has also been established that arsenate is adsorbed at a faster rate than arsenite (Moore and Pierce, 1982; Hering and Wilkie, 1996; Hering *et al.* 1996; Hering *et al.* 1997). The kinetics of arsenate adsorption and coprecipitation on the surface of ferrihydrite were studied by Fuller *et al* (1993) who found that the process is diffusion controlled. The removal of arsenic (pH 6-8) through coprecipitation with ferrihydrite has been determined by Merrill *et al.* 1986 (pH 6-8) and Dimitrova *et al.* 1992 (pH 5) to be semi-quantitative. This semi-quantitative removal has also been established for arsenic in geothermal waters at pH 4-5 (Buisson *et al.* 1979).

The drinking water industry has utilised the adsorption and coprecipitation of arsenic species with ferrihydrite to improve the quality of drinking water (Jekel, 1994; Edwards, 1994; Driehaus *et al.* 1995; Anderson and Fergusson, 1974; Edwards and McNeill, 1997; Hering *et al.* 1997; Edwards and McNeill, 1995; Hering *et al.* 1996; Edwards and McNeill, 1997). It has also been shown that sand coated with iron(III) oxide removes arsenite and arsenate from drinking water (Chaudhuri and Joshi, 1996).This has been proposed as a method for processing drinking water in developing countries to WHO recommended levels.

Natural organic matter (NOM) in fresh waters is composed of three fractions, which are defined according to their solubilities in acids and bases. Fulvic acids (FA's) are soluble both in acid and alkaline solutions and have the lowest molecular weights (~ 500 to 1500 g/mol). Humic acids (HA's) are soluble in alkaline solutions (they have dissociable hydroxyl and carboxyl groups), but are insoluble in acid below pH 2, and have molecular weights of ca 10,000-50,000 (Rubin, 1976). Humin is insoluble in acid and alkaline solutions and has the highest molecular weights. The pK_a values for humic and fulvic acids are above 1.5 (Powell and Fenton, 1996). In fresh waters fulvic acids constitute ~ 60% of NOM. Fulvic and humic acids play a major role in the transport and deposition of arsenic. This is through arsenate binding to metals such as Fe and Al that are also complexed to the fulvic and humic acids (Aiken *et al.* 1979; Langmuir, 1997; Hart and

Davies, 1978; Bourg, 1988). Fulvic acids are known to interact strongly with amorphous iron hydroxides (Hart and Davies, 1978). The stability of the complexes formed varies with the pH or E_h of the water (Rubin, 1976). NOM and oxyhydroxides can also coat suspended particulate matter and therefore adsorb anions or cations depending on the chemical nature and pH of the surface (Forstner, 1989). The writer is not aware of other published data on the adsorption of arsenate and arsenite to ferrihydrite in the presence of humic substances.

Other ions can compete with arsenic for the binding sites on ferrihydrite (Hart and Davies, 1978). It has been established that sulfate (Peng and Pingkuan, 1994; Hering and Wilkie, 1996) and phosphate (Peng and Pingkuan, 1994) ions have an inhibiting effect on the adsorption of arsenate to ferrihydrite.

5.2 SCOPE OF THIS WORK

This section of work was concerned with establishing the interaction of arsenate with ferrihydrite in the absence and presence of other ions. It will be shown (Chapter 7) that arsenate is the major arsenic species arising from leaching of mine waste. Therefore this work has involved simulating the interaction of arsenate from mine derived leachates with ferrihydrite, which is also a product of AMD. The pH of 4.7 has been used to mimic the pH in the AMD situation. One important competing ion is sulfate, another component from AMD. Calcium arises from the dissolution of limestone which could be used to control AMD. Fulvic (FA) and humic acids (HA) are natural products leached from the soils into fresh water streams. Arsenic from the AMD is likely to interact with them indirectly through their association with ferrihydrite.

The objectives of studies with ferrihydrite were concerned with establishing:

i) the effect of pH on adsorption of arsenate on ferrihydrite,

ii) the removal/complexation of arsenate from solution by FA, HA and by FA-Fe(III) and HA-Fe(III) complexes.

iii) the competitive effect of FA, HA and FA-Fe(III) and HA-Fe(III) complexes, and elevated levels of sulfate or calcium, on the adsorption of arsenate on ferrihydrite.

These objectives were achieved by:

i) assessing the effect of pH on arsenate adsorption on ferrihydrite (pH 3-9) using batch experiments where arsenate and ferrihydrite were equilibrated then the supernatant solution analysed for non-bound arsenate.

ii) assessing the competitive effect of FA, HA and FA-Fe(III) and HA-Fe(III) complexes, and elevated levels of sulfate or calcium, on the adsorption of arsenate on ferrihydrite. This was done by conducting batch experiments (pH 4.7) as for (i) but also containing fulvic acid, humic acid, Fe(III)-humic complexes, sulfate or calcium.

5.3 EXPERIMENTAL

5.3.1 Humic and Fulvic acids

This sub-section describes the preparation of HA-Fe(III) colloids, and their interaction with arsenate in the presence or absence of sulfate and calcium. Similar experiments involving fulvic acid are described in section 3.3.2.1. Arsenate was determined by the HG-GFAAS method described in section 2.3.4.

Part A: HA-Fe(III) solutions

i) Solutions containing 0, 50, 80, 150 and 300 μg/L Fe(III) and 84 mg/L HA were prepared by adding 16.8 mg of HA to a series of Fe(III) solutions, making them up to 200 mL with Milli-Q water and adjusting to pH 2.0 with HCl (BDH-Aristar).

ii) The pH of each of the above solutions (i) was raised slowly to 4.7 by addition of acetate buffer. The solution was stirred throughout the procedure.

iii) To determine the amount of Fe complexed to colloidal HA, 1 mL aliquots were filtered (0.025 μm) and the Fe in the filtrate was measured by GFAAS as described in section 2.3.3.

Part B: Adsorption of As(V) to HA-Fe(III) colloids

i) The solutions from Part A were filtered (0.025 μm), the filtrate was discarded and the residue was washed with Milli-Q water.

ii) Each residue was placed in 200 mL of Milli-Q water (stirred) at pH 4.7. To these solutions, arsenate was added to give a final arsenate concentration of 0, 100, 150, 250 and 400 ppb in 200 mL.

iii) The solutions from (ii) were allowed to equilibrate overnight and 2.5 mL aliquots of the solution were filtered (0.025 μm) and the filtrate analysed for non-adsorbed As(V).

Part C: Desorption of AsO_4^{3-} by Ca^{2+} and SO_4^{2-}

i) The desorption of As(V) from the HA-Fe(III)-As(V) colloidal complex was investigated in two 200 mL solutions. This involved preparation of fresh 200 mL HA-Fe(III)-As(V) colloidal solutions following similar procedures to these in Part A and Part B (i-ii). However this experiment involved fixed Fe(III) and As(V) concentrations of 500 and 400 μg/L respectively. Then calcium and sulfate ions were added respectively to give final concentrations of 20 ppm for each ion in 200 mL. The As(V) adsorption was monitored as in step B(iii) over a period of 24 h.

Part D: Competitive adsorption of Ca^{2+}, SO_4^{2-} and AsO_4^{3-} to the HA-Fe(III) colloidal complex

i) A 200 mL HA-Fe(III) colloidal solution was prepared with final concentrations of 500 μg/L Fe(III) and 84 mg/L humic acid (similar to Part A (i)) then allowed to equilibrate for 2 days.

ii) The solution from (i) was filtered (0.025 μm) and the residue washed with Milli-Q water. The residue was then added to 200 mL of solution containing 500 ppb As(V), sulfate (20 ppm) and calcium (20 ppm). The experiment was allowed to proceed for 24 h during which 2 mL aliquots were sampled, filtered (0.025 μm) and measured for As(V).

5.3.2 Amorphous Ferric Hydroxide (ferrihydrite-FeO(OH)(s))

This subsection deals with the synthesis of FeO(OH)(s). Then it describes the procedures taken to investigate:

i) the effect of pH on arsenate adsorption to FeO(OH)(s)

ii) the rate of arsenate adsorption to FeO(OH)(s) at pH 4.7.

iii) the effect of competing ions on arsenate adsorption to FeO(OH)(s) at pH 4.7.

a) Preparation of ferrihydrite

Amorphous iron(III) hydroxide was prepared for arsenate adsorption experiments. The method of preparation was adapted from Pierce and Moore (1982). It involved addition of 25 mL of 1 M NaOH (BDH-Analar) to 1.665g of ferric sulfate (BDH-Analar) dissolved in 200 mL of Milli-Q water and allowing the solution to stand for 30 minutes. Then the suspension was filtered (0.025 μm) and the retentate washed several times with Milli-Q water. The colloid was then suspended in 200 mL of Milli-Q water to give a final concentration of 4.45 g $Fe(OH)_3$ per liter of solution.

i) All subsequent adsorption studies used a ferrihydrite concentration of 4.45 mg/L with ionic strength 0.1M ($NaNO_3$).

b) Effect of pH on As(V) adsorption

Batch adsorption experiments were conducted with 100 mL solutions containing 4.45 mg/L ferrihydrite (0.1 M $NaNO_3$), and 200 ppb of As(V) at pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0. The pH was adjusted with 1 M HNO_3 (BDH-Analar) and 1 M NaOH (BDH-

Analar). The solutions were allowed to equilibrate overnight then filtered through 0.025 μm membrane filters. The filtrates were analysed for non-adsorbed arsenate.

c) Rate of arsenate adsorption to ferrihydrite at pH 4.7

A 500 mL solution containing 4.45 mg ferrihydrite per liter was buffered to pH 4.7 (0.1 M acetate) and 1 ppm of As(V) was added to the stirred suspension. Aliquots were taken at intervals over 120 min, filtered (0.025 μm) and measured for non-adsorbed arsenate.

d) The effect of competing ions on arsenic adsorption at pH 4.7

Solutions were prepared as in 5.3.2(c) but in addition to 1 ppm arsenate they contained one of the following:

i) 200 ppm sulfate
ii) 800 ppm Ca^{2+}
iii) 17 mg/L fulvic acid (FA)
iv) 84 mg/L humic acid (HA)
v) FA-Fe(III) complex
vi) HA-Fe(III) complex

Each solution was sampled at intervals up to 120 min, filtered (0.025 μm) and analysed for non-adsorbed arsenate by HG-GFAAS.

5.4 RESULTS AND DISCUSSION

5.4.1 Humic and fulvic acids

The dominant arsenate species at pH 4.7 is $H_2AsO_4^-$ (Dzombak and Morel, 1990). Its interaction with HA-Fe(III) can be represented by the following equation:

$$R\text{-}Fe(OH)^{2+} + H_2AsO_4^- = R\text{-}Fe\text{-}OAsO_3H^+ + H_2O \qquad (5.8)$$

R is the humic acid

The results for the interaction of arsenate with Fe(III) bound to humic acid are given in Table 5.1. They indicate that the amount of arsenate bound depends on the amount of Fe(III) initially bound to the humic acid. The data are consistent with a 1:1 interaction between the arsenate and the Fe(III) bound to the humic acid. This has also been established in the work on fulvic acids in Chapter 3. Prior to arsenate adsorption, the uptake of Fe(III) to humic acid was quantitative.

The adsorption of As(V) to the HA-Fe(III) colloid was not affected by calcium or sulfate ions (results not shown). Calcium adsorption would not be favoured because of the net positive charge on the Fe centre in HA-Fe(III) at pH 4.7. One can infer that the sulfate adsorption is much weaker than arsenate adsorption.

Table 5.1: The interaction of arsenate with Fe(III) bound to humic acid in 200 mL solutions (pH 4.7).

*Fe(III) (μmoles)	#AsO_4^{3-} (μmoles)
0	0
0.18	0.24
0.27	0.33
0.5	0.37
1.03	0.99

* is Fe(III) complexed to HA; # is arsenate bound to the HA-Fe(III) colloidal complex.

5.4.2 Amorphous ferric hydroxide (ferrihydrite)

5.4.2.1 The effect of pH on adsorption of As(V) onto ferrihydrite

The dominant arsenate species are $H_2AsO_4^-$ at pH 2-7, and $HAsO_4^{2-}$ at pH 7-11 (Dzombak and Morel, 1990). The adsorption of arsenate therefore can be represented by the following equations:

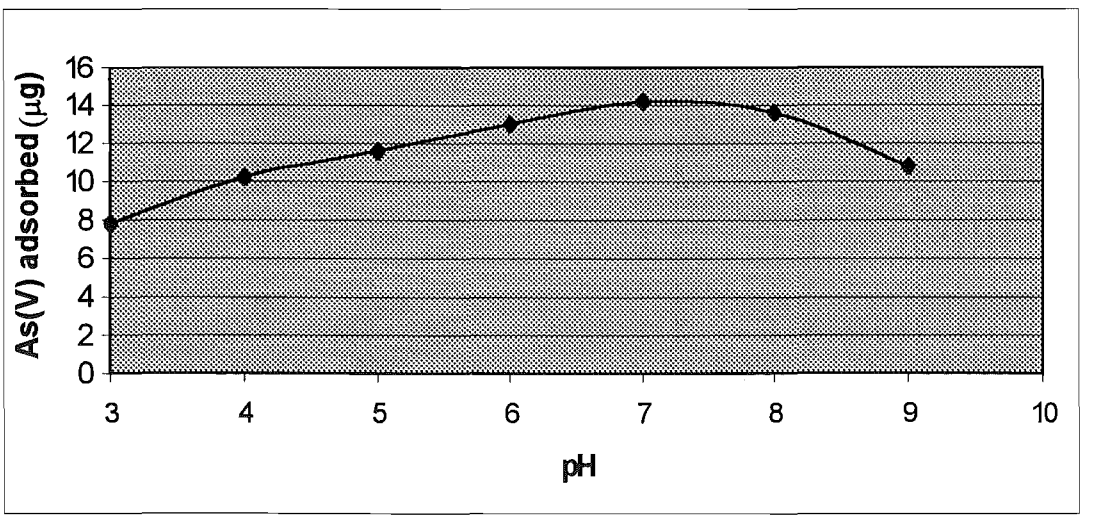
$$\equiv Fe\text{-}OH + H_2AsO_4^- = FeOAsO_3^{2-} + H_2O + H^+ \qquad (5.9a)$$

$$\equiv Fe\text{-}OH + HAsO_4^{2-} = FeOAsO_3^{2-} + H_2O \quad (5.9b)$$

The adsorption of arsenate is electrostatically favoured at pH values less than the pH_{zpc} (~8.1) of ferrihydrite. Above pH 8.1, there is a net negative surface charge and therefore adsorption is expected to be lower.

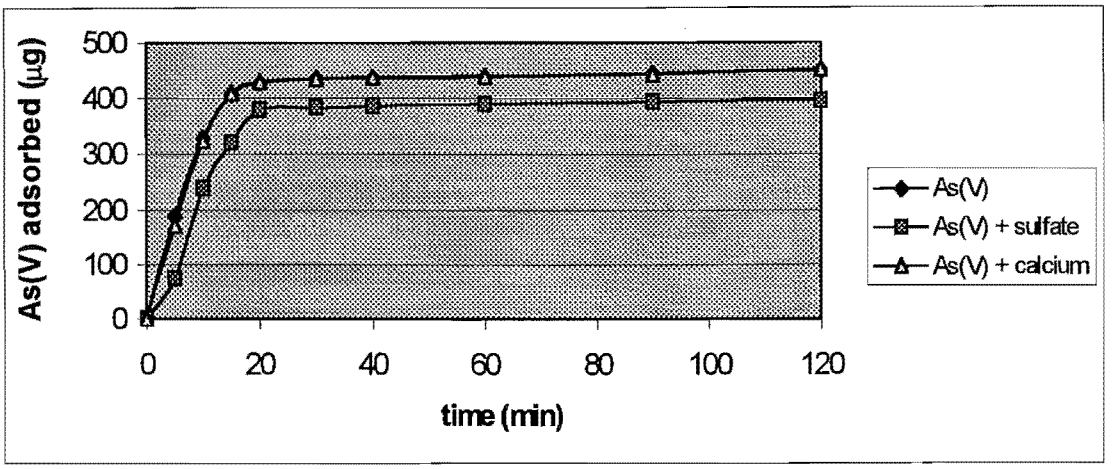
Figure 5.1 shows the experimentally determined adsorption of arsenate as a function of pH. The maximum adsorption occurs near pH 7, suggesting that adsorption of $HAsO_4^{2-}$ dominates due to its high charge. At lower pH where the surface charge is greater, adsorption is less, presumably because $H_2AsO_4^-$ adsorbs more weakly. At pH 7.0, the point of maximum adsorption, 71 % (14.2 μg) of As(V) was adsorbed by 445 μg ferrihydrite from a 100 mL solution containing 200 μg/L of As(V).

Figure 5.1: The effect of pH on the adsorption of arsenate (200 μg/L) on ferrihydrite (4.45 mg/L).



5.4.2.2 The effect of competing ions on arsenate adsorption to ferrihydrite

Figure 5.2: The effect of 800 ppm calcium and 200 ppm sulfate on arsenate (1 ppm) adsorption onto ferrihydrite at pH 4.7 in a 500 mL solution.



Arsenate ion ($H_2AsO_4^-$) adsorbs onto ferrihydrite according to reaction 5.9a. As shown in Figure 5.2, equilibrium is reached within 30 min of contact with the ferrihydrite. The equilibrium state corresponds to absorption of 445 µg of arsenate (of a total 500 µg) onto 2.22 mg of FeOOH. The high efficiency of this reaction indicates that high concentrations of Fe(III) from the AMD discharge could promote the removal of arsenate through its interaction with ferrihydrite formed by Fe(III) hydrolysis and precipitation.

Co-occurring solutes such as sulfate compete with the adsorption of arsenate to ferrihydrite. This can be represented by the surface complexation reaction:

$$\equiv FeOH + SO_4^{2-} + H^+ = \equiv FeSO_4^- + H_2O \qquad (5.10)$$

The extent of this competition is indicated by the results in Figure 5.2 for a ferrihydrite suspension in a solution containing 200 ppm sulfate and 1 ppm arsenate. Because of the competitive adsorption of sulfate, only 75 % of the As(V) is adsorbed in the presence of SO_4^{2-} compared to 90% in the absence of sulfate. In contrast, there was no competitive

effect from calcium, presumably because of the positive charge on the adsorbent at pH 4.7. It is possible that calcium would interact with the ferrihydrite only at a pH above pH_{zpc}, where the net charge on the reactive surface is negative.

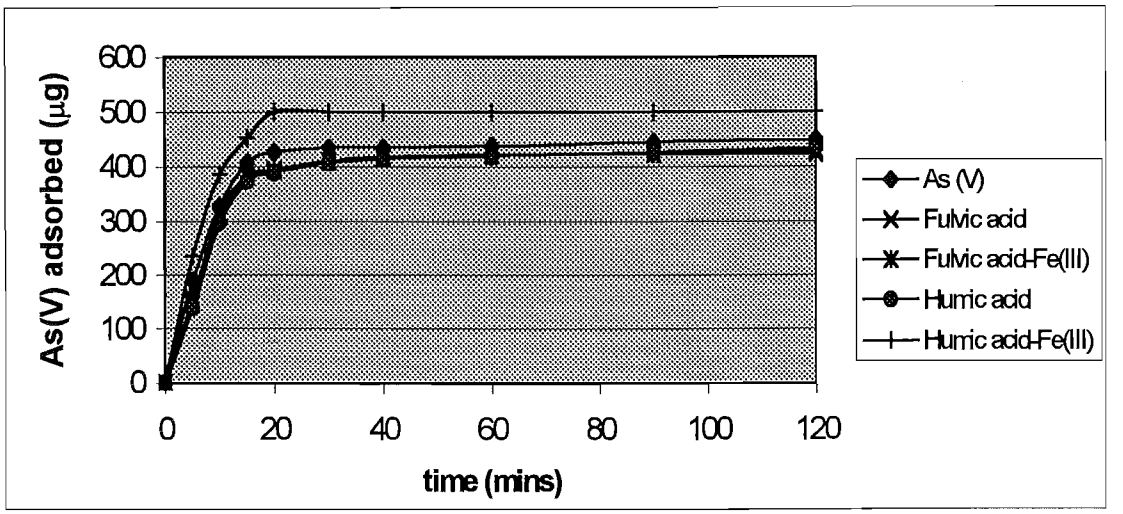
Table 5.2: The effect of FA, HA, FA-Fe(III) and HA-Fe(III) on the adsorption of arsenate 1 (ppm) to ferrihydrite at pH 4.7. The values shown are μg As(V) adsorbed.

	μg As(V) adsorbed				
Time (min)	**HFO**	**FA**	**FA-Fe(III)**	**HA**	**HA-Fe(III)**
0	0	0	0	0	0
5	188	145	153	138	234
10	329	309	313	295	387
15	407	383	383	374	453
20	427	395	394	390	500
30	435	411	410	408	500
40	436	419	417	414	500
60	438	421	422	420	500
90	445	424	423	427	500
120	449	428	423	434	500

Solution volume of 500 mL contains a total of 500 μg As(V) and 2.22mg FeOOH. HFO is ferrihydrite, FA is fulvic acid and HA is humic acid.

The effects of FA, HA, FA-Fe(III) and HA-Fe(III) on the adsorption of arsenate to ferrihydrite at pH 4.7 are shown in Table 5.2 and Figure 5.3. Fulvic acids (FA) had a slight (5 %) inhibiting effect on the adsorption of arsenate. The FA adsorbs onto the ferrihydrite because of the FA negative charge formed by the deprotonation of the functional groups. It can therefore compete with arsenate for adsorption to ferrihydrite. The soluble FA-Fe(III) complex also reduces the arsenate adsorbed. It does this by interacting with arsenate to form the stable complex FA-Fe(III)-As(V), thus competing with colloidal ferrihydrite for the arsenate.

Figure 5.3: The effect of FA, HA, FA-Fe(III) and HA-Fe(III) on the adsorption of arsenate 1 (ppm) to ferrihydrite at pH 4.7 in 500 mL.



Humic acid (HA) inhibited arsenate adsorption by only 3%. Its mode of action would be similar to that of fulvic acid. However in the presence of a HA-Fe(III) complex there is 100% arsenate removal after 20 minutes. The net removal of arsenate can be explained by the combination of the reactions given in equations 5.8 and 5.9 viz. Complex formation and adsorption. Any As(V) bound to HA-Fe(III) is not detected in the analysis of the filtrate since HA-Fe(III) is an insoluble phase which is retained on the 0.025 µm membrane filter during the analysis of the aliquots of taken for arsenic determination.

5.5 CONCLUSION

Ferrihydrite semi-quantitatively and rapidly removes arsenate from solution. It therefore means that under an AMD situation where ferrihydrite is present, arsenate can be removed through interaction with colloidal iron(III) oxyhydroxides. The arsenate adsorption is inhibited by competing ions in the following order: sulfate > FA ≅ HA. Complexes of HA-Fe(III) and FA-Fe(III) bind arsenate as 1:1 complexes through the

Fe(III). The reaction of arsenate with HA-Fe(III) gives another mechanism for removal of arsenate from solution because the HA complex is insoluble in acidic conditions.

CHAPTER 6

CHARACTERISATION AND REACTIVITY OF WASTE ROCKS

This Chapter reports the characterisation and reactivity of waste rocks. The emphasis is on the AMD-producing sandstone.

6.1 INTRODUCTION

Sulfide containing mine waste rocks can generate acidity, hence giving rise to AMD. At the Macraes mining site the dominant rock type is carbonate-bearing and is weakly basic. A minor constituent, a sandstone closely associated with gold bearing quartz seams is strongly acidic and contains reactive forms of pyrite. Therefore, leaching studies in this work involved the sandstone waste rock, which has the greater potential for generating AMD. This Chapter provides a physical and chemical description of the sandstone and basic rock and identifies the products of sandstone leaching under oxic and anoxic conditions.

6.2 SCOPE OF THIS WORK

As a preliminary step to subsequent column leaching experiments (Chapter 7), this Chapter presents a detailed analysis and petrographical description of the sandstone waste rock.

The objectives of this work were to establish:

i) The mineralogical properties of the sandstone and basic rock (GB 13).

ii) The effect of O_2 concentration on the sandstone leaching rates and products.

iii) The product ratios from leaching/oxidation of the sandstone (total Fe/sulfate, As(III)/As(V), Fe(III)/Fe(II), and total As/sulfate).

These objectives were achieved by:

i) Characterising sandstone fractions by microscopic examination.

ii) Measuring XRF and XRD spectra.

iii) Examining the petrography of the sandstone.

iv) Leaching the sandstone under oxic and rigorously anoxic conditions, followed by the determination of total Fe, sulfate, As(III)/As(V), Fe(III)/Fe(II) in leachate solutions.

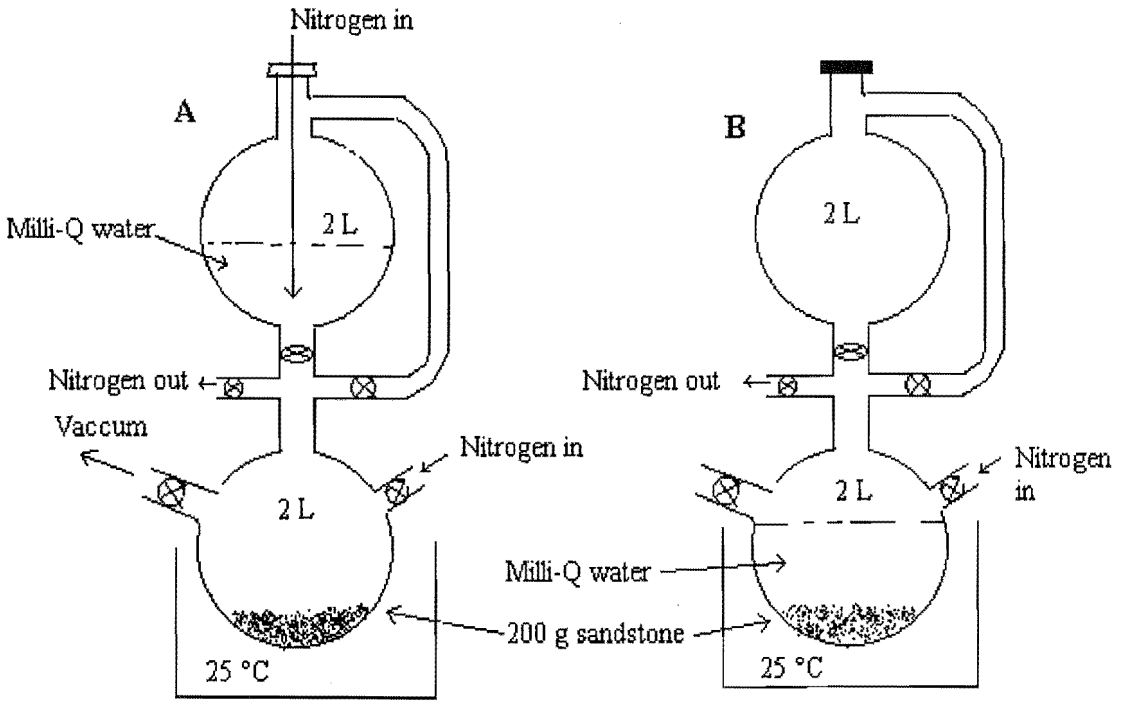
6.3 EXPERIMENTAL

Batch leaching of the sandstone was conducted under oxic and rigorously anoxic conditions (excluding bacteria e.g. *T. ferroxidans*). To achieve this, 200 g (1-10 mm particle size) of the sandstone was leached over 96 hr in a 2 L flask with 2000 mL of Milli-Q water. Details of the oxic and anoxic leaching were as follows:

i) Anoxic leaching. All air was evacuated from the 200 g sample contained in the round bottom flask. This was followed by purging the flask with oxygen free N_2. This cycle was repeated 5 times. Milli-Q water in the upper compartment of the apparatus was also purged with nitrogen gas (2 h) (see diagram A in Figure 6.1). Then the oxygen free Milli-Q water was drained into the flask containing the solid sample and the leaching commenced under a nitrogen atmosphere (see diagram B in Figure 6.1).

ii) Oxic leaching. This involved leaching 200 g of the sandstone waste rock with 2000 mL of Milli-Q water. This was performed whilst air was purged through the flask. Solutions were manually stirred after sampling in both experiemnts.

Figure 6.1: Schematic diagram of apparatus for the anoxic leaching of the sandstone. Diagram (**A**) shows the evacuation and purging of O_2 with N_2. Diagram (**B**) shows the leaching of the sandstone under a N_2 atmosphere.



For each experiment, 10 mL aliquots were sampled at various time intervals during the course of the leaching up to 96 h, and the pH was measured with the instrumentation described in section 2.3.1.2. The samples were then membrane filtered (0.025 μm) and stored for subsequent analyses of sulfate, Fe(III)/Fe(II) and As(III)/As(V). The samples were not acidified because the acidic nature of leachates (~ pH 3.0) warranted no further acidification before storage.

Ion chromatography (described in section 2.3.7) was used to monitor the release of sulfate from the sandstone. Fe(II) was measured as the red-orange iron (II)-orthophenanthroline complex as described in section 2.3.2. Fe(III) was calculated from the difference after the addition of 10% ascorbic acid to reduce all Fe(III) to Fe(II) and determining by the same method. The redox (E_h) potentials were evaluated through

calculation of the Fe(II)/ Fe(III) redox couple using the Nernst equation. All arsenic measurements were made using the HG-GFAAS method described in section 2.3.4.

Spot tests were made on separate sandstone fractions to identify the fraction (Table 6.1) responsible for the sandstone acidity. The fractions were obtained or separated based on their colouration. These tests were performed by addition of Milli-Q water to grains of the sandstone. pH was determined by use of pH sensitive indicator paper (3-7, 1-14) and by use of the pH indicators: methyl red, methyl orange and bromo-phenol blue.

External facilities were used for XRF, petrographic and XRD analysis. These facilities are described in sections 2.3.16.2, 2.3.16.3 and 2.3.16.4 respectively.

6.4 RESULTS AND DISCUSSION

The emphasis was on the sandstone because of its reactivity and contribution to AMD. However for completeness a petrographic and XRF analysis has been included for the waste rock, GB 13.

6.4.1 Solid state properties

6.4.1.1 Microscopic examination

Different fractions of the sandstone were identified and characterized according to descriptions outlined in Table 6.1. All fractions generated an acidic solution (pH ~ 3) within seconds of contact with Milli-Q water. Also observed were rounded translucent quartz particles as the dominant component in each fraction. This product indicates very strong weathering under acid conditions (pH < 4). No fraction demonstrated discernible magnetic properties.

Table 6.1: Physical characterisation of the sandstone waste rock.

Fraction	Description
Fraction 1	Grayish color, crystals yellowish brown under microscopic examination. Crystals caused slight polarisation of light.
Fraction 2	Yellowish powder crumbles under thumb pressure. Crystals polarized light.
Fraction 3	Hard reddish orange brown crystals.

6.4.1.2 XRD-powder diffraction

The fractions in Table 6.1 were submitted for XRD analysis. Results showed that there was very little difference between the major minerals in fractions 1, 2 and 3. The patterns were dominated by quartz and illite. Iron oxide coatings were observed in fraction three. However, the XRD lines were very weak, suggesting either very low concentrations or low crystalinity.

6.4.1.3 Petrographic descriptions (Sandstone and GB 13)

a) Sandstone

Samples found to consist of particles of vein breccia composed mainly of rounded clasts of vein quartz, greywacke and minor pyrite in a matrix of sericite/illite, chlorite, quartz, titanite and minor carbonate. Some of the vein clasts, especially the larger ones, contain minor amounts of pyrite, arsenopyrite, stibnite and bournonite. In addition, the petrographic examination established that:

i) Carbonate, occurring as scattered grains, made up <1% in the thin sections examined.

ii) Pyrite occurs mainly as cubic grains in several grain sizes; 0.005-0.05 and 0.2-0.7 mm.

iii) Arsenopyrite is more localised as small (0.005-0.1 mm in length) acicular crystals.

iv) Stibnite (SbS_3) and bournonite (Cu_5FeS_4) occur locally along grain boundaries and late fractures in vein quartz.

v) The greywacke clasts are considerably veined and recrystallised, especially by comparison with a greywacke sample.

vi) Several particles were locally oxidised, with matrix impregnated along the late fractures by limonite ($2Fe_2O_3.3H_2O$) or jarosite ($K[Fe(SO_4)_2Fe(OH)_3]$).

b) GB 13

GB 13 is carbonate bearing, and the predominant rock type is an unfoliated, medium-grained, poorly sorted, subangular, greywacke sandstone. A few particles of weakly foliated, moderately sorted, siltstone are also present. The main components are:

i) quartz grains (ave. 38%)

ii) matrix (ave. 28.6%)

iii) micas (ave. 19.2%)

iv) carbonate (ave. 13.3%)

v) sulfides (ave. 0.4%)

Pyrite, as the dominant sulfide mineral, is mainly in fine grained (~0.01 mm) crystals. A few larger crystals (0.1-0.2 mm) and aggregates of pyrite are present in siltstone particles. The only arsenopyrite observed was as fine acicular crystals in a carbonate vein. Minor (~1%) graphite occurs as discrete clasts (~0.1 mm) in the greywacke sandstone.

6.4.1.4 X-ray fluorescence (XRF) - Sandstone and GB 13

Tables 6.2 and 6.3 show the major elements and the minor elements respectively. Of significance are the results for arsenic. They indicate 15,000 μg As/g (1.5%) present in the sandstone. In comparison, only 62 μg As/g was detected in the GB 13 rock. The petrographic observations indicated that the arsenic compound in the sandstone is arsenopyrite.

Table 6.2: Major elements by XRF

Compound	Sandstone (%)	GB 13 (%)
SiO_2	69.58	72.42
TiO_2	0.66	0.59
Al_2O_3	14.48	9.98
Fe_2O_3	4.26	3.99
MnO	<0.01	0.06
MgO	0.81	2.29
CaO	0.14	1.74
Na_2O	<0.1	<0.1
K_2O	2.76	2.13
P_2O_5	0.15	0.19
LOI*	3.10	6.49
Total	95.89	99.86

*LOI is loss on ignition

Table 6.3: Minor elements by XRF.

Element	Sandstone (μg/g)	GB 13 (μg/g)
As	15,000 (1.5%)	62
V	103	72
Cr	65	54
Ni	7	25
Zn	38	59
Zr	206	277
Nb	13	12
Ba	<20	359
La	36	36
Ce	1249	83
Nd	50	50
Ga	26	12
Pb	854	6
Rb	158	104
Sr	124	80
Th	14	13
Y	38	30

6.4.2 Leaching properties

6.4.2.1 Spot tests: Acidity tests, E_h [(Fe(III)/Fe(II)]

The sandstone fractions (Table 6.1) were tested for acid generation on contact with water. All fractions showed an acidic pH. Bromo-phenol blue and methyl red indicated a pH of 3.0. All three fractions give instant acidity on addition of Milli-Q water.

Using the Nernst equation, E_h values were calculated from the Fe(III) and Fe(II) concentrations measured after 96 h leaching, for both oxic and anoxic conditions. The E_h values under oxic and anoxic conditions were 820 mV and 750 mV vs. SHE respectively. These values were similar to that measured in column leaching experiments (Chapter 7) from which it is inferred that the experimental E_h was largely influenced by the iron redox couple. The different E_h values resulted from the presence or absence of O_2, affecting the Fe(II)/Fe(III) ratio.

Table 6.4: The E_h values calculated from the Fe(II) and Fe(III) concentrations in sandstone leachate at 96 h (under oxic and anoxic leaching conditions).

Leaching conditions	Fe(II) μg/g	Fe(III) μg/g	E_h/mV
Oxic	20	125	820
Anoxic	34	18	750

6.4.2.2 Batch leaching

a) Fe (III) and Fe(II)

Results in Figures 6.2a and 6.2b show that the concentrations of the Fe(III) species leached from the sandstone under oxic conditions were greater than those for leaching under anoxic conditions. It is inferred that the availability of dissolved oxygen under oxic

conditions contributed to the increased oxidation of pyrite (hence total Fe produced) and to the oxidation of Fe(II) to Fe(III).

Results shown in Figure 6.2b suggest that the initial surge in Fe(III) concentration under anoxic conditions arose from oxidised ferric products present on the sandstone surface (e.g. limonite and /or jarosite). These form during the prior exposure of the sample to atmospheric oxygen. The oxidised surface products are also expected to contribute to the rapidly generated acidity of the sandstone (6.4.2.1). After depletion of the surface Fe(III) species under anoxic conditions, oxidation of the pyrite presumably proceeds as in equation 1.5. Under oxic conditions, the reactions shown in equations 1.1 and 1.2 will also be operative.

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1.1)$$

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \quad (1.2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (1.5)$$

Figure 6.2a: Fe(III) and Fe(II) leached under oxic conditions.

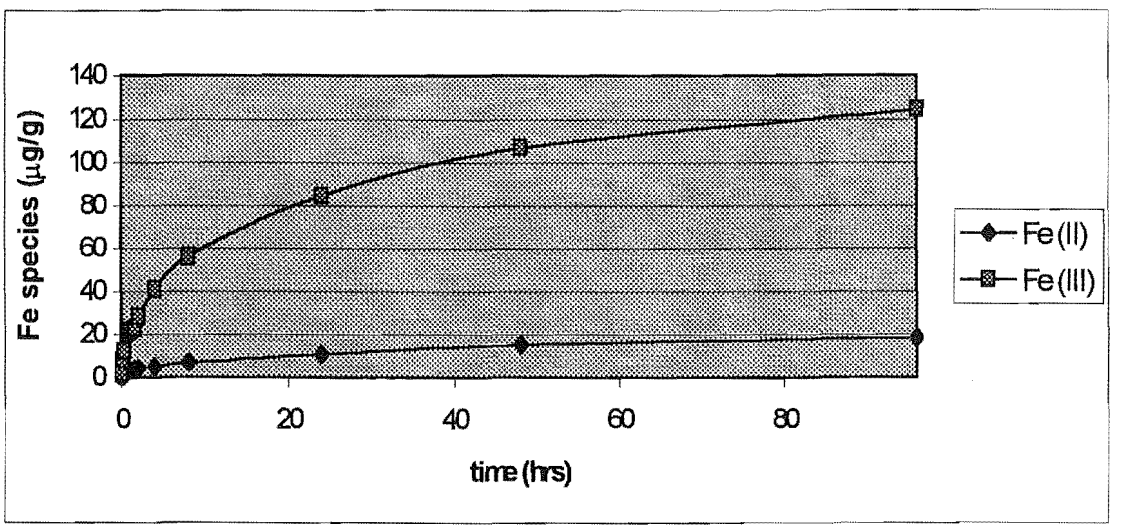
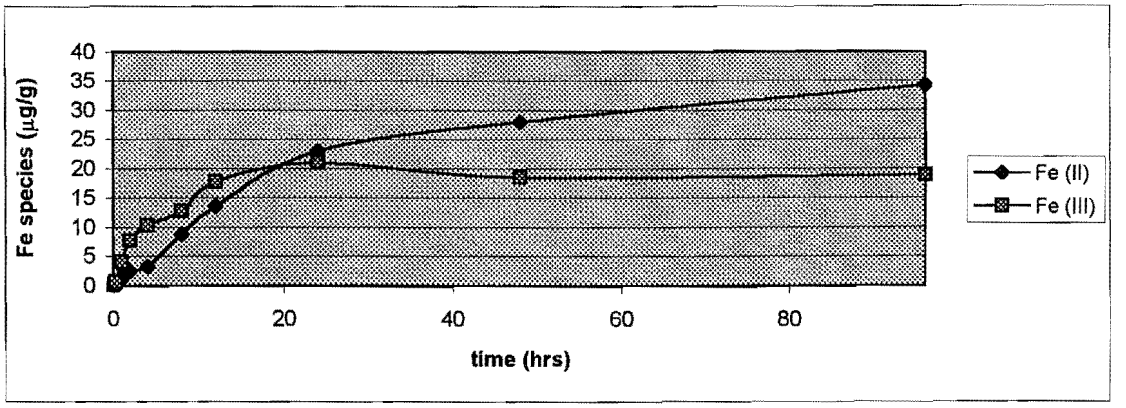


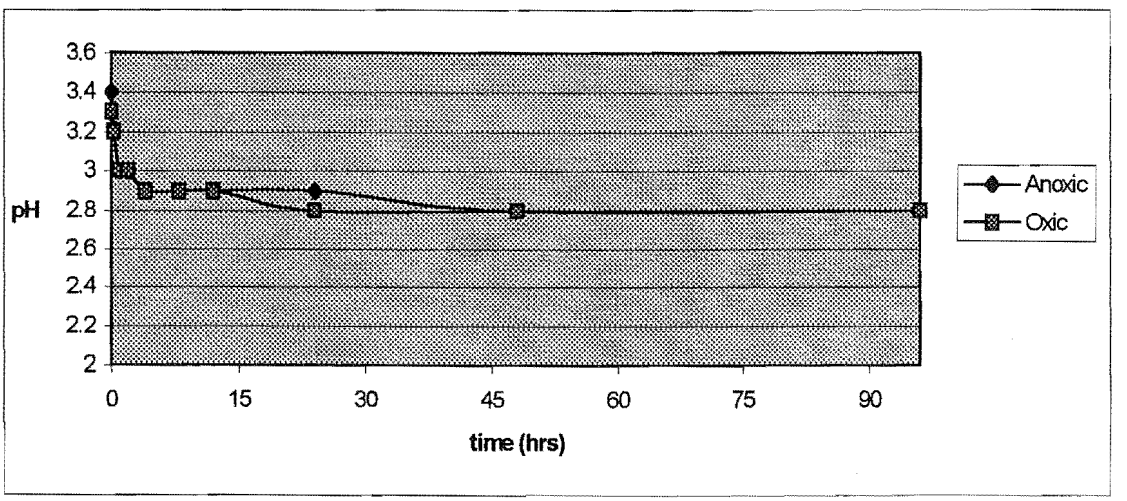
Figure 6.2b: Fe(III) and Fe(II) leached under anoxic conditions.



b) pH

The pH of the leachates (Figure 6.3) was similar under both oxic and anoxic conditions. The low pH can be attributed to oxidation products (e.g. jarosite) leached from the surface of the sandstone.

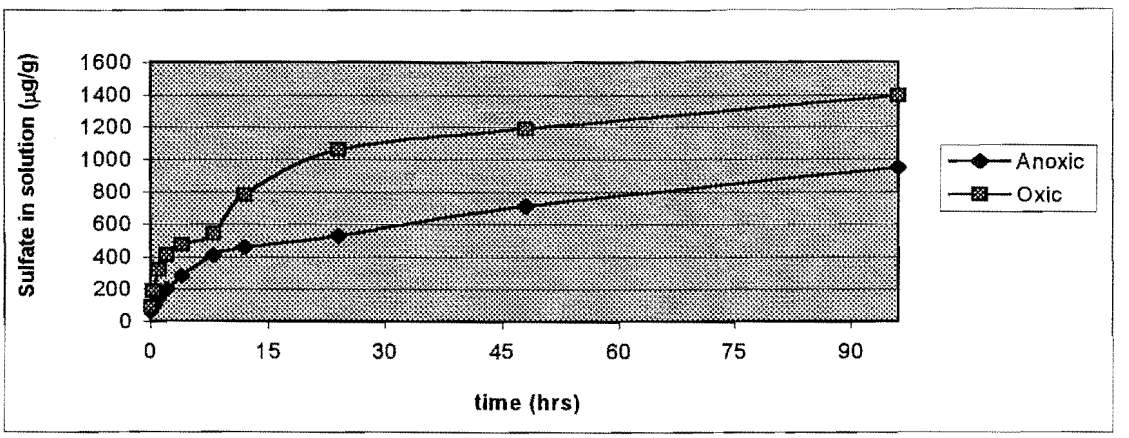
Figure 6.3: pH of leachate under both oxic and anoxic conditions.



c) Sulfate

Figure 6.4 shows that sulfate, an oxidation product of both pyrite and arsenopyrite, is produced at a higher rate under oxic than anoxic conditions. This implies that the rate of pyrite oxidation is enhanced by dissolved oxygen. However, by reference to figure 6.1a it could be inferred that the role of O_2 is to convert Fe(II) to Fe(III), which is an effective oxidising agent for pyrite.

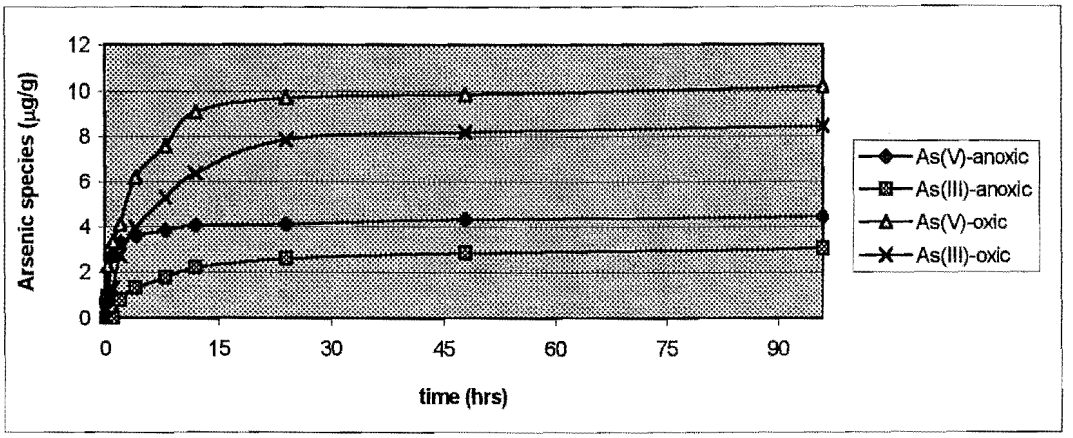
Figure 6.4: Sulfate in leachate under both oxic and anoxic conditions



d) Arsenate and arsenite

Figure 6.5 shows that the concentrations of arsenate and arsenite produced from sandstone leaching are both increased in the presence of dissolved oxygen. These species are largely derived from the oxidation of arsenopyrite. The As(V):As(III) ratios were 1.2:1.0 for oxic and 1.4:1.0 for anoxic conditions. The lower ratio under oxic conditions may be due to the greater adsorption of As(V) on $Fe(OH)_3$ precipitates, than under anoxic conditions. More Fe(III) forms in the presence of O_2 (compare Figures 6.2a and b) and hence more precipitated material is expected providing a larger surface area for As(V) adsorption.

Figure 6.5: Arsenate and arsenite leached from sandstone under oxic or anoxic conditions.



e) Product ratios

Most work to date on acid mine drainage has discussed the release of acid in the form of sulfuric acid, to the environment. For this work, arsenic is the primary concern, and the role of Fe in controlling arsenic availability is also of interest. Hence the ratios of soluble $Fe:SO_4^{2-}$ and $As:SO_4^{2-}$ were examined. Figure 6.6a shows that the amount of soluble Fe in leachates is very small compared to that of sulfate. Presumably Fe precipitates as insoluble hydroxides and would largely remain associated with the waste rock stack. Figure 6.6b shows the amount of soluble As in the sandstone leachate is also small compared to the amount of sulfate. This ratio must reflect the relative amount of pyrite and arsenopyrite in the sandstone, the relative reactivities of each mineral and immobilisation of As on insoluble hydroxides.

Figure 6.6a: Total iron to sulfate ratio under oxic and anoxic leaching.

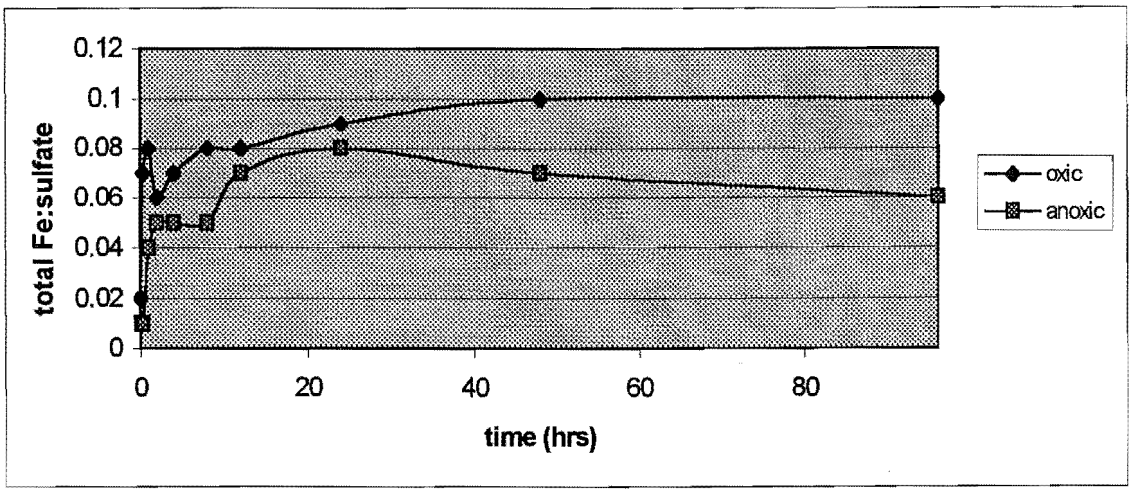
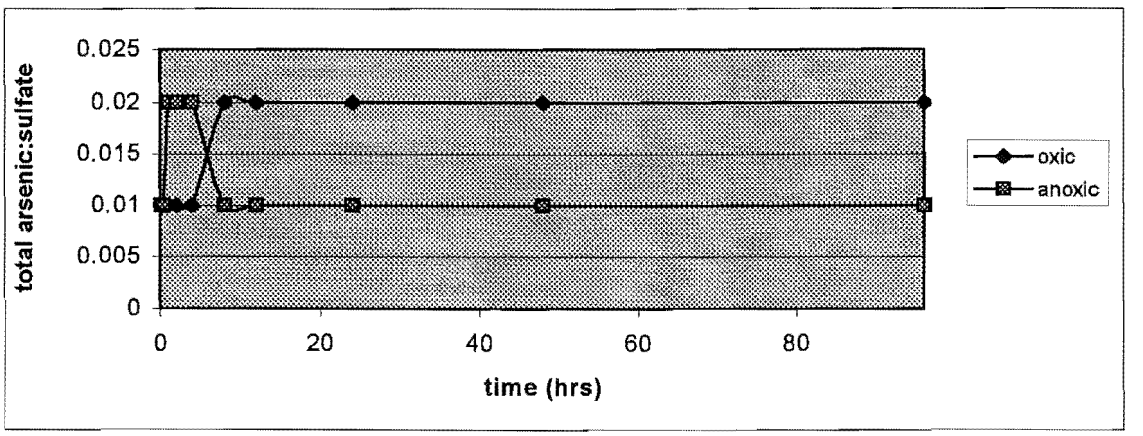


Figure 6.6b: Total arsenic to sulfate ratio under oxic and anoxic conditions



6.5 CONCLUSION

The sandstone waste rock contains both pyrite and arsenopyrite and generates an acidic pH of 2.8. The acidity could be a result of surface oxidation products e.g. ferric salts and jarosite. The presence of oxygen increases the Fe(III)/Fe(II), total Fe/sulfate and total

As/sulfate ratios. Furthermore, oxygen gives rise to Fe(III) dominance under oxic environment, whereas Fe(II) dominates under anoxic conditions.

Considering the concentrations of Fe, SO_4^{2-} and As in solution, it is apparent that the rate of increase slows significantly. For SO_4^{2-} which is expected to be highly soluble in the leached solution this decrease must correspond to a decrease in the rate of dissolution from the rock. It is proposed that a passivating coats the rock surface, slowing down dissolution. This layer is most likely $Fe(OH)_3$. For Fe and As, there may be a combination of reduced rate of dissolution and precipitation or adsorption (for Fe and As respectively). This is discussed further in Chapter 7.

CHAPTER 7

MINE WASTE ROCKS: COLUMN LEACHING EXPERIMENTS

This Chapter deals with leaching simulation of mine waste rocks and gives the measurements of leaching products (e.g. arsenic). The results are used to compare with data in Chapter 8 concerning the control of arsenic with limestone.

7.1 INTRODUCTION

In a mining scenario, waste rock stacks containing reactive sulfides will produce acid mine drainage (AMD) upon contact with water. Waste rocks stacks are a common practice in the mining industry for storage of waste rocks. These usually contain regions which are oxic (upper) and anoxic (lower). As the AMD percolates through successive zones in the stack the quality of the AMD may be affected through changes in its chemical composition. The chemical and physical properties of the waste rocks will affect the quality of the AMD that is formed, as well as changes in quality over time.

Leaching experiments have been designed to closely simulate actual weathering conditions which would be encountered in a waste rock stack at the proposed mine site. Oxic type experiments simulate the upper region whereas anoxic experiments the lower regions of the waste rock stack. Non-recycled leachate experiments were conducted to simulate the weathering of rocks in the upper layer of the waste rock stack whereas recycled leachates simulated leaching in the lower regions.

7.2 SCOPE OF THIS WORK

7.2.1 Objectives

The objectives of leaching experiments in these investigations were to:

i) Simulate the leaching of mine waste rocks GB 13 and sandstone using a variety of leachants applicable to the field.

ii) Quantify the Fe, As(III)/As(V), heavy metals and acidity in the leachates.

7.2.2 Strategy/methodology

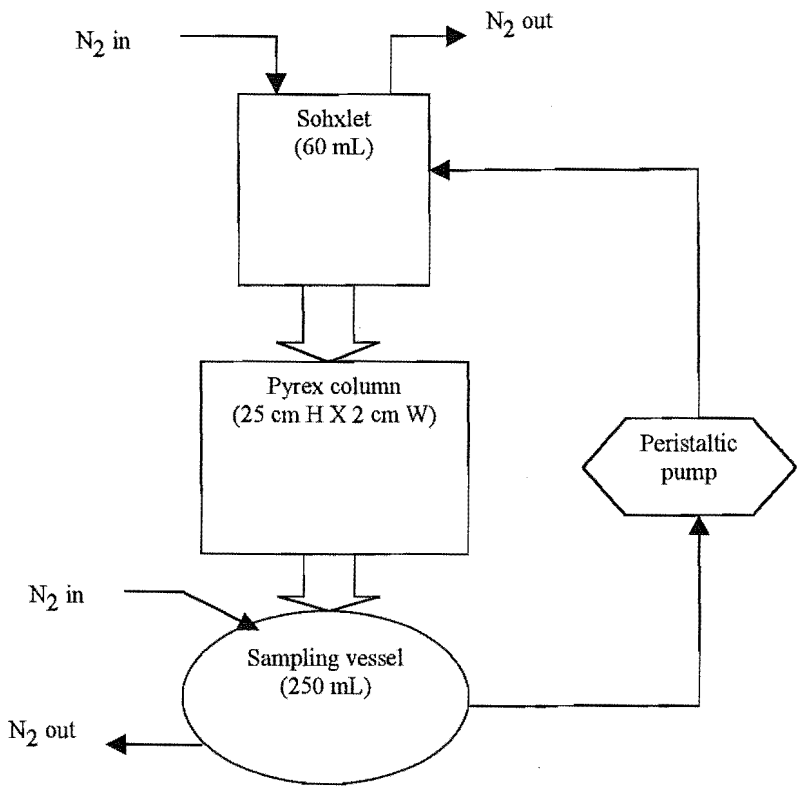
The objectives in section 7.2.1 were achieved using recycled and non-recycled Milli-Q, rain and humic water leachates under anoxic and oxic conditions. After leaching, the leachates were measured for Fe, As(III)/As(V), heavy metals and acidity. The effect of pH on waste rock dissolution was studied using acetate and ammonium buffers.

7.3 EXPERIMENTAL

7.3.1 Kinetic leaching columns

Kinetic leaching tests were conducted using six Pyrex glass columns of 25 cm height and 2 cm diameter. The columns were specially designed to fit sohxlet extractors, which function as reservoirs for recycled leachates. To the sohxlets and columns $N_2(g)$ inlets and outlets were incorporated for conducting anoxic leaching (see Figure 7.1 below). Oxic leaching was conducted by leaving the column and receiving vessels exposed to atmospheric oxygen.

Figure 7.1: A flow chart representing the leaching apparatus used in anoxic and oxic leaching experiments. N_2 was not used for oxic leaching experiments.



Leaching tests were conducted on the particle size fraction (1-10 mm) on two waste rock types provided by the mining company. The samples were a rock with the identification GB 13 and a sandstone type waste rock. The amounts of sample leached were 65 g for GB 13 and 50 g for the sandstone. The quantity of the samples introduced into the columns was governed by two factors: the amount of arsenic detectable by the analytical method used and the height of sample in the column. The sample height was chosen so that the particle size (based on the maximum particle size of 10 mm) was 8% of the sample height in the column. Such a percentage best represents the actual particle size to height ratio most likely to be encountered in the waste rock stack.

7.3.2 Leaching solutions

Leaching solutions used were Milli-Q, rain and humic water. The rain and humic (pH 6.9) waters were sampled from the proposed mining site. Leaching with humic water is important to mimic possible seepage of dissolved organic matter from adjacent vegetation into the waste rock stack. Rain water was used to mimic the effect of leaching by localised rainfall.

The effect of pH on leaching products of GB 13 was studied by passing 0.1M acetate (pH 5.0) and 0.1 M ammonium buffers (pH 8.5) over the GB 13 waste rock. The buffers were prepared according to the following procedures:

i) The acetate buffer was prepared by weighing 2.051 g of sodium acetate (BDH-Analar) and making up to ~200 mL with Milli-Q water, then adding concentrated acetic acid (BDH) dropwise until pH 5.0. Then the final solution was made up to 250 mL with Milli-Q water.

ii) The ammonium buffer was prepared by weighing 1.337 g of ammonium chloride (BDH-Analar) and making up to ~200 mL with Milli-Q water then adding potassium hydroxide pellets (BDH-Analar) until pH 8.5. Then the final solution was made up to 250 mL with Milli-Q water.

These leaching tests were conducted in the dark and under oxic and anoxic conditions. The dark mimicked lighting conditions in the interior of the waste rock stack. The volume of leachant passed through each column each day was 120 mL. This equates to 4 years of precipitation at the mine site when continually leaching for 15 days.

At specified time intervals *in situ* measurements were made for pH, E and conductivity using the procedures outlined in Chapter 2. Sampling was conducted for Fe and arsenic analysis by taking 2 mL aliquots. These samples were filtered through 0.45 μm then 0.025 μm membrane filters. Total Fe and the arsenic speciation were measured by the methods outlined in sections 2.3.3 and 2.3.11 respectively.

7.3.3 Recycled and non-recycled leaching

Under recycled leaching, leachates were collected in the sampling vessel, then recycled by pumping with a peristaltic pump to a sohxlet at the top of the column. After 12 hours 60 mL of the leachate was again discharged into the column from the sohxlet. For non-recycled leaching, fresh leachants were introduced into the column daily, followed by sampling of the resultant leachate. The remaining leachate was acidified to pH 2.0 (BDH-Aristar) and stored (4 °C). Prior to each non-recycled leaching the leachant was bubbled with N_2 for 1 h.

7.3.4 Method validation

There were two aspects of validation of the leaching methods that were utilised in these experiments. These were;

i) leaching reproducibility.

ii) the effect of sample storage on arsenic speciation.

Leaching reproducibility experiments were conducted to check on the variability of measured parameters: As(V)/As(III), total soluble Fe, conductivity, pH and E_h. To achieve this non-recycled Milli-Q water was passed through three leaching columns containing samples of GB 13. These were operated under similar oxic conditions, sample weight, height and volume of leachant as described in section 7.3.

The effect of sample storage on arsenic speciation was studied by leaching 50 g of sandstone for 30 minutes with 100 mL of Milli-Q water, then filtering through a 0.025 μm membrane filter and storing the filtered solution at 4 °C. The solution was sampled at various time interval by taking 1 mL aliquots, acidifying to pH 2.0 with HCl (BDH-Aristar) and analysing for As(V) and As(III) using the HG-GFAAS method described in section 2.3.11. The measurements were made to establish whether the arsenic speciation had changed over a period of 14 days before batches were analysed for arsenic.

7.4 RESULTS

All data for concentrations of As and metals in leachates are expressed as either μg per g of rock or μg per mL of leachate. For all leaching experiments a yellow brown precipitate collected on the frit at the bottom of the leaching column and it was assumed to be $Fe(OH)_3(s)$. This was not studied but it could have had a significant role in adsorption of As species from leachates before they reached the collection vessel.

The initial datum point (day 0) on each Figure (or data set) corresponds to the initial measurement made after addition of the first batch of leachant.

7.4.1 Method validation

7.4.1.1 Leaching reproducibility

Non-recycled Milli-Q water (under oxic conditions) was passed through GB 13 samples contained in three different columns. The measured arsenic species are given in Figures 7.2a-c, total soluble Fe (Figure 7.3), pH, E_h and conductivity (Table 7.1).

Figure 7.2a: Arsenic from 65 g of GB 13 leached with non-recycled Milli-Q water (column 1).

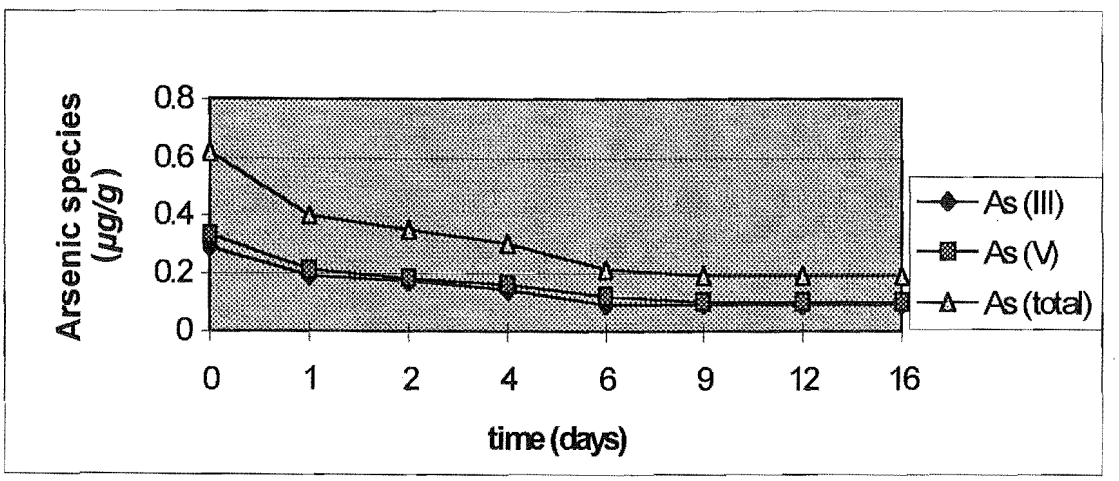


Figure 7.2b: Arsenic from 65 g of GB 13 leached with non-recycled Milli-Q water (column 2).

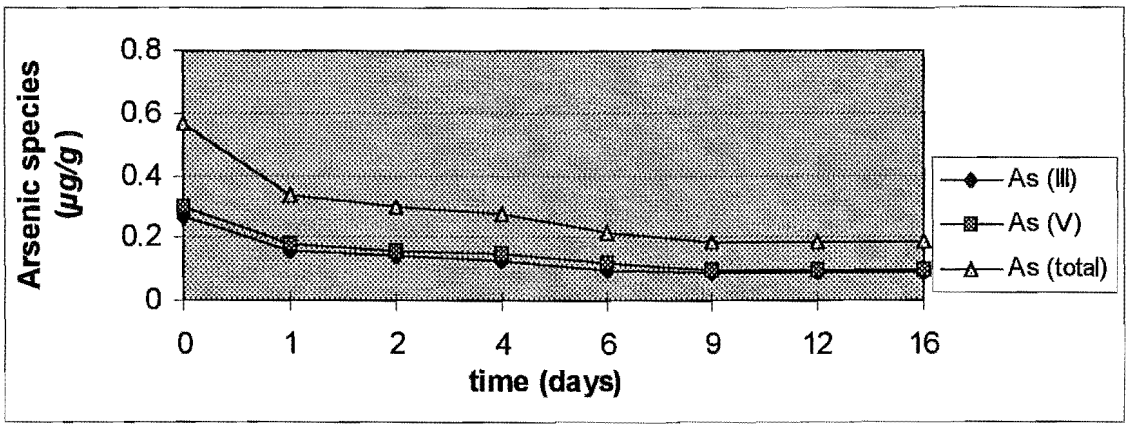


Figure 7.2c: Arsenic from 65 g of GB 13 leached with non-recycled Milli-Q water (column 3).

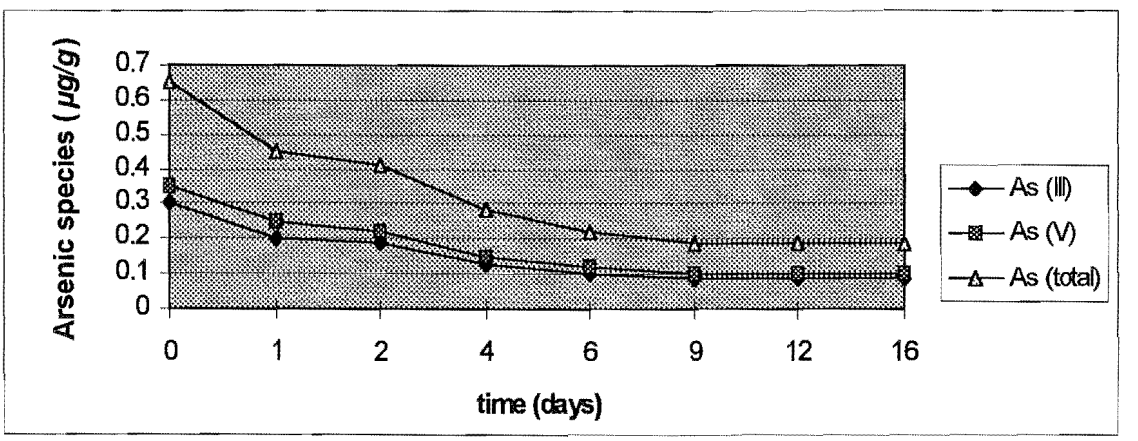


Figure 7.3: Total iron from 65 g of GB 13 leached with non-recycled Milli-Q water.

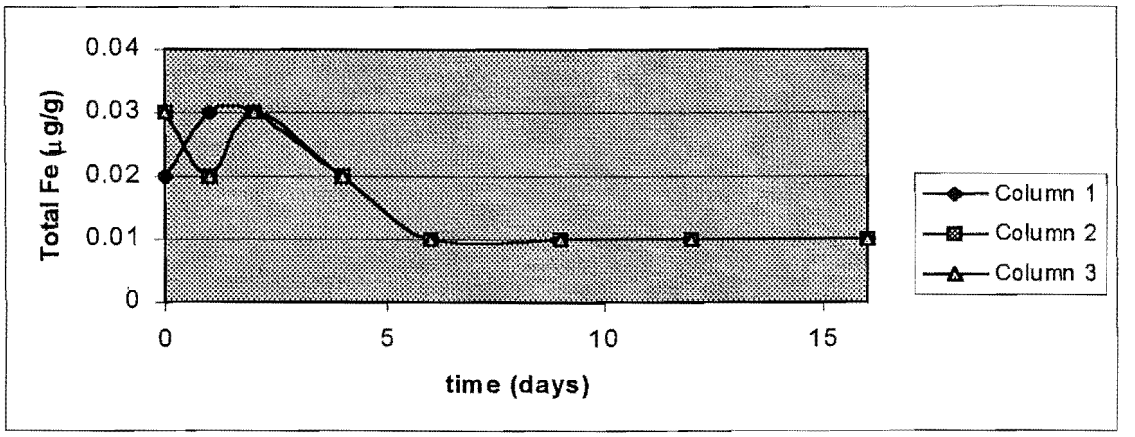


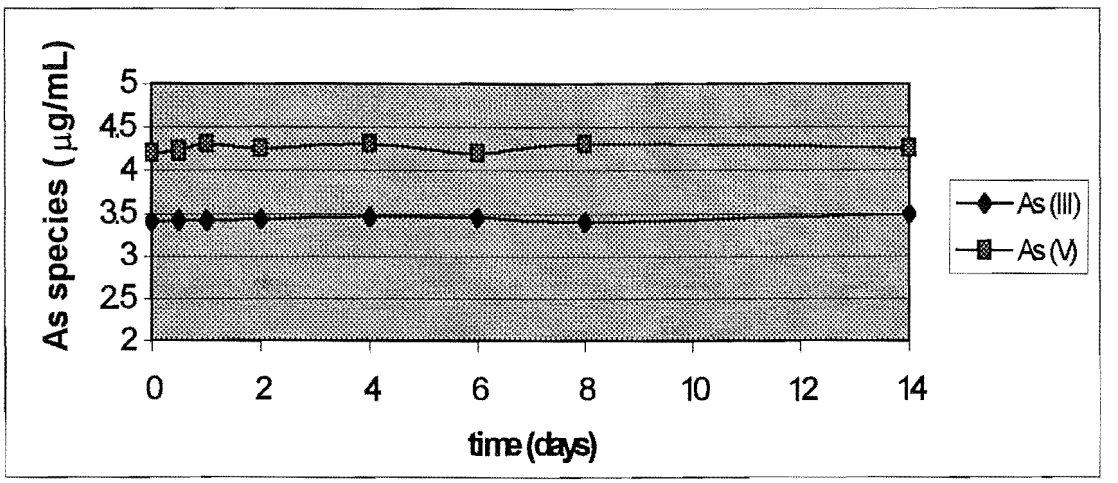
Table 7.1: The pH, E and conductivity of leachate from GB 13 leached with non-recycled Milli-Q water under oxic conditions. The results shown are mean values for 65 g of GB 13 leached in three columns and the errors expressed are the standard deviation from the mean.

Parameter	Day 0	Day 4	Day 16
pH	7.37 ± 0.17	7.04 ± 0.15	6.80 ± 0.16
E (*mV vs. SCE*)	243 ± 3	172 ± 4	167 ± 7
Conductivity (*µS/cm*)	55 ± 8	17 ± 3	12 ± 4

7.4.1.2 Effects of sample storage on arsenic speciation

Leachate samples from the sandstone were stored for 14 days and As(III) and As(V) measured to monitor changes in arsenic speciation during storage. The results are given in Figure 7.4.

Figure 7.4: The effect of leachate age on arsenic speciation.



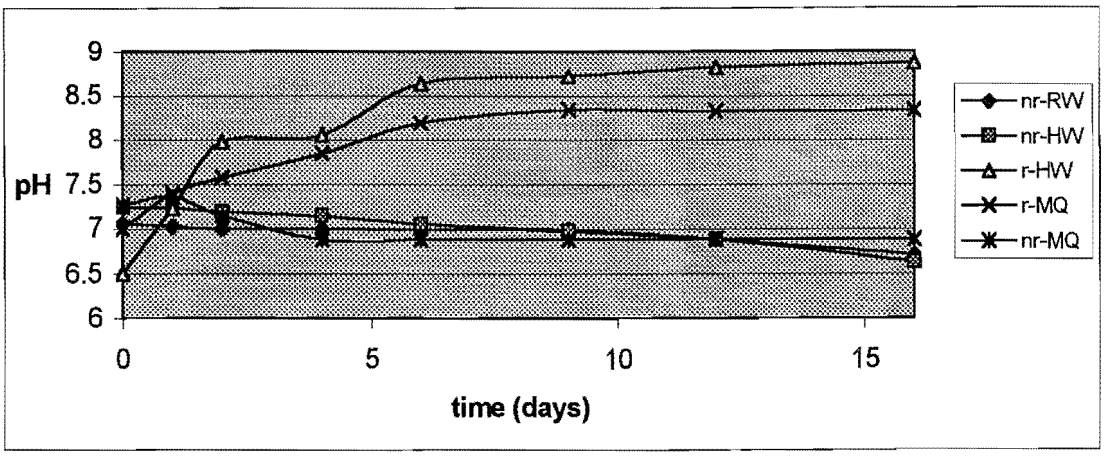
7.4.2 Basic rock (GB 13)

7.4.2.1 Anoxic leaching

Leaching was effected under cycled and non-recycled conditions, using Milli-Q water, rain water and humic water (pH 7.1) as leachants under anoxic conditions. The results are given in the following sections for pH (Figure 7.5), As(V) and As(III) (Figures 7.6a-e), total Fe (Figure 7.7), E (Figure 7.8) and ASV-labile metals (Table 7.2).

a) pH

Figure 7.5: The pH of leachates from 65 g of GB 13 leached with recycled and non-recycled leachates under anoxic conditions.



nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; r-HW is recycled humic water, r-MQ is recycled Milli-Q water and nr-MQ is non-recycled Milli-Q water.

b) As(V) and As(III)

Figure 7.6a: Arsenic species leached from 65 g of GB 13 with non-recycled Milli-Q water under anoxic conditions.

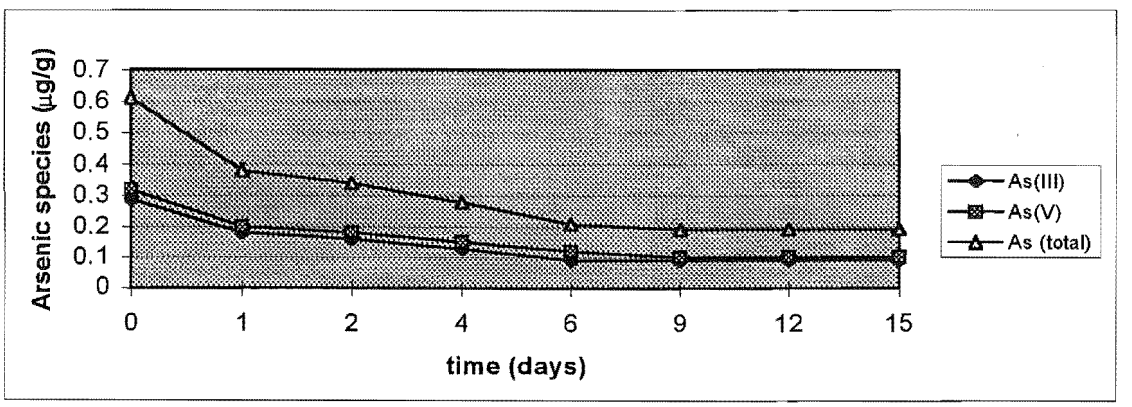


Figure 7.6b: Arsenic species leached from 65 g of GB 13 with recycled Milli-Q water under anoxic conditions.

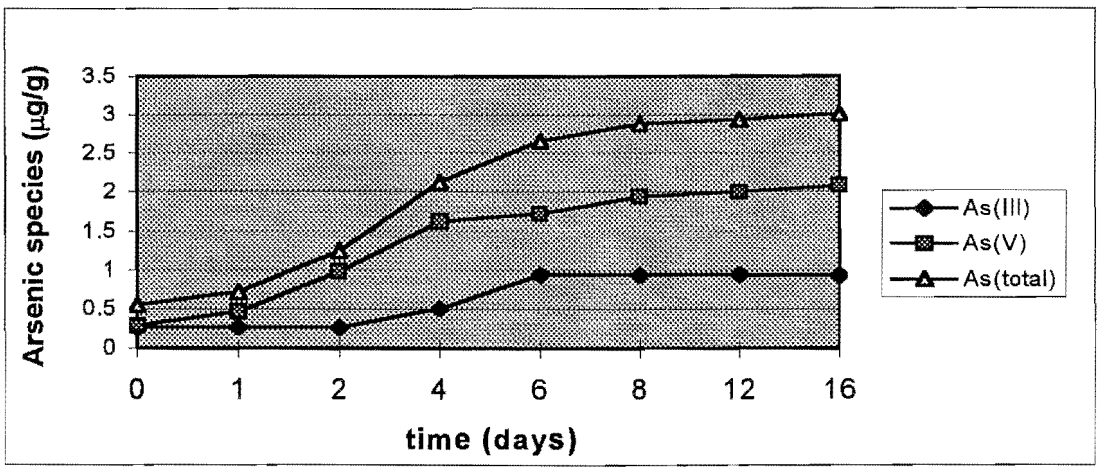


Figure 7.6c: Arsenic species leached from 65 g of GB 13 with non-recycled humic water under anoxic conditions.

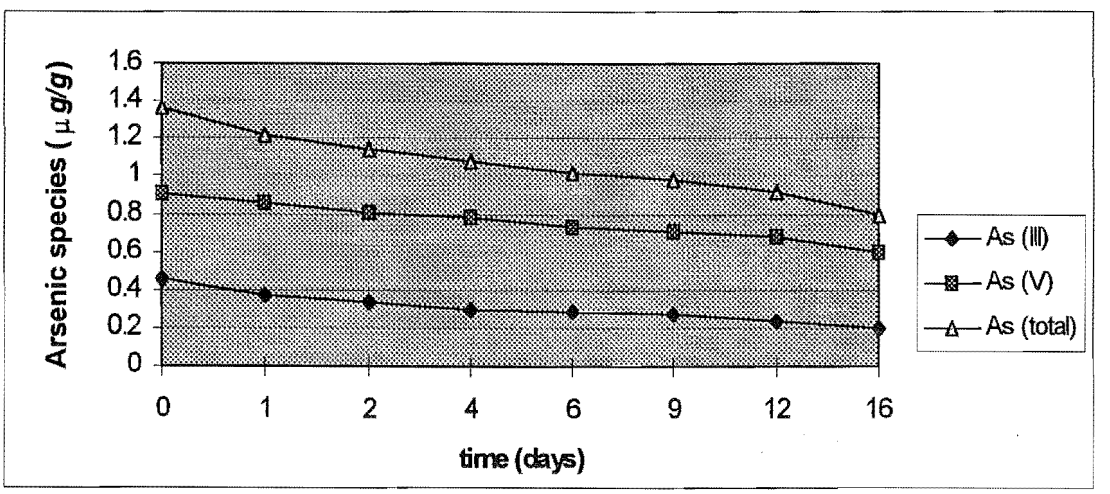


Figure 7.6d: Arsenic species leached from 65 g of GB 13 with recycled humic water under anoxic conditions.

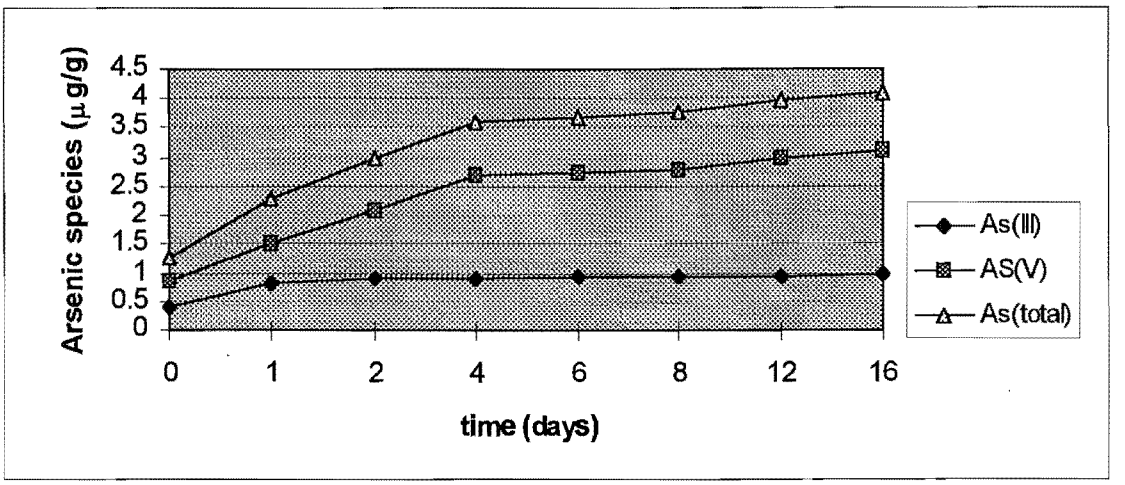
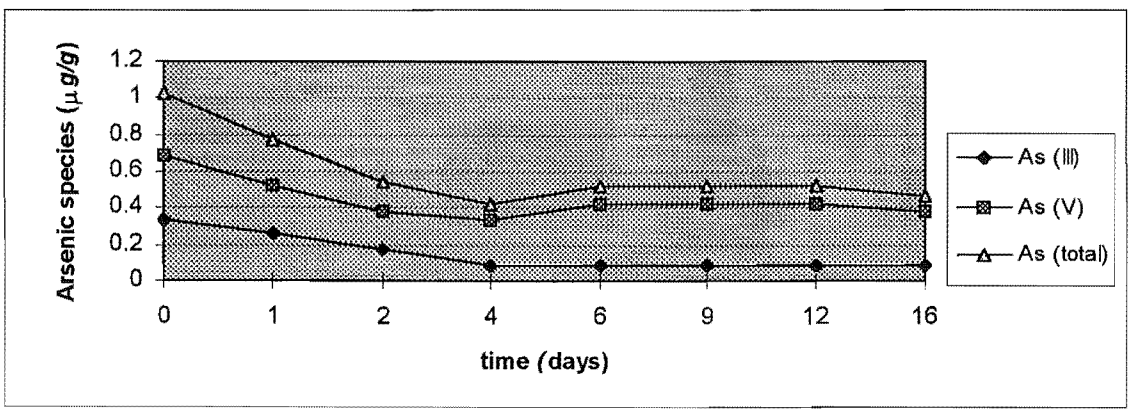
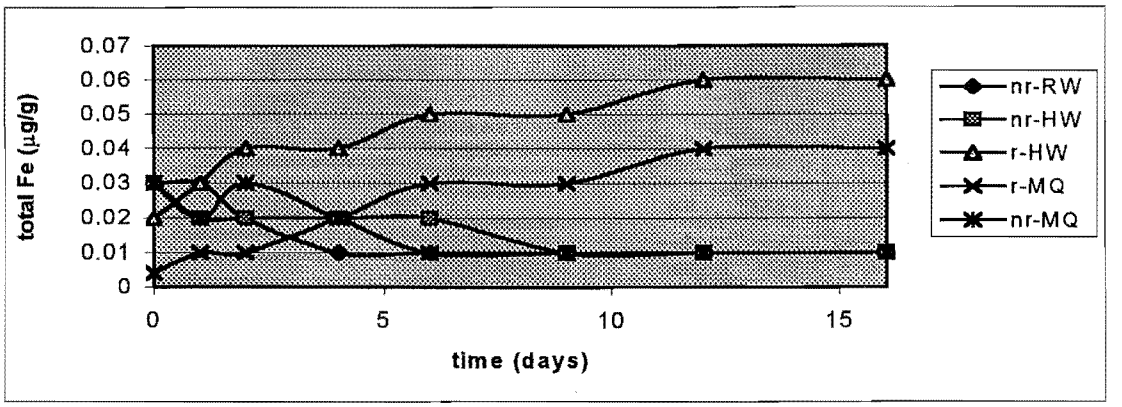


Figure 7.6e: Arsenic species leached from 65 g of GB 13 with non-recycled rain water under anoxic conditions.



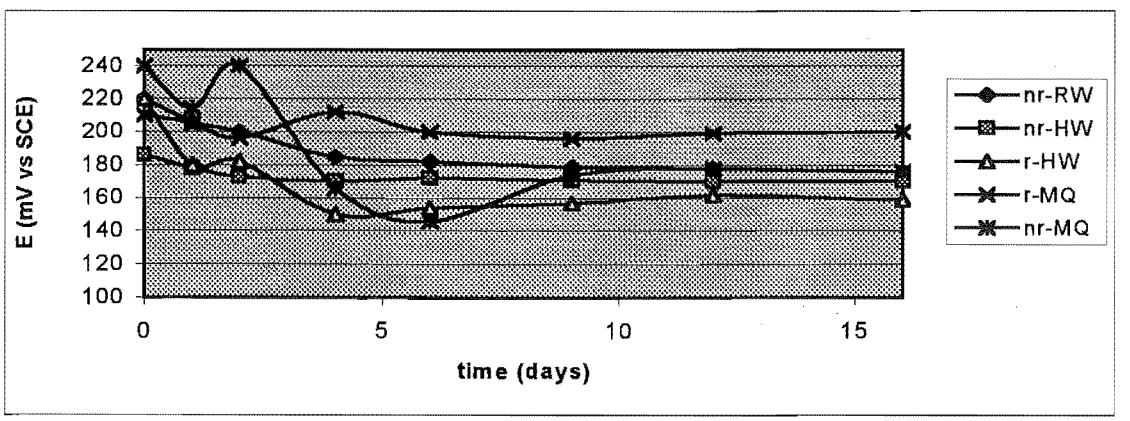
c) Total Fe and E

Figure 7.7: Total Fe in leachates recycled and non-recycled over 65 g of GB 13 under anoxic conditions.



nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; r-HW is recycled humic water, r-MQ is recycled Milli-Q water and nr-MQ is non-recycled Milli-Q water.

Figure 7.8: E of leachates recycled and non-recycled over 65 g of GB 13 under anoxic conditions.



nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; r-HW is recycled humic water, r-MQ is recycled Milli-Q water and nr-MQ is non-recycled Milli-Q water.

d) ASV-labile metals

Table 7.2: The ASV-Labile metals from non-recycled leachates passed over 65g of GB 13 under anoxic conditions.

Leachate	Cu (μg/g)		Pb (μg/g)		Cd (μg/g)		Zn (μg/g)	
	0 d*	16 d#	0 d	16d	0 d	16 d	0 d	16 d
Milli-Q	0.001	0.001	0.003	0.001	0.001	0.001	0.002	0.001
Rain	0.001	0.003	0.004	0.001	0.04	0.001	0.03	0.01
Humic	0.005	0.006	0.01	0.001	0.04	0.001	0.002	0.001

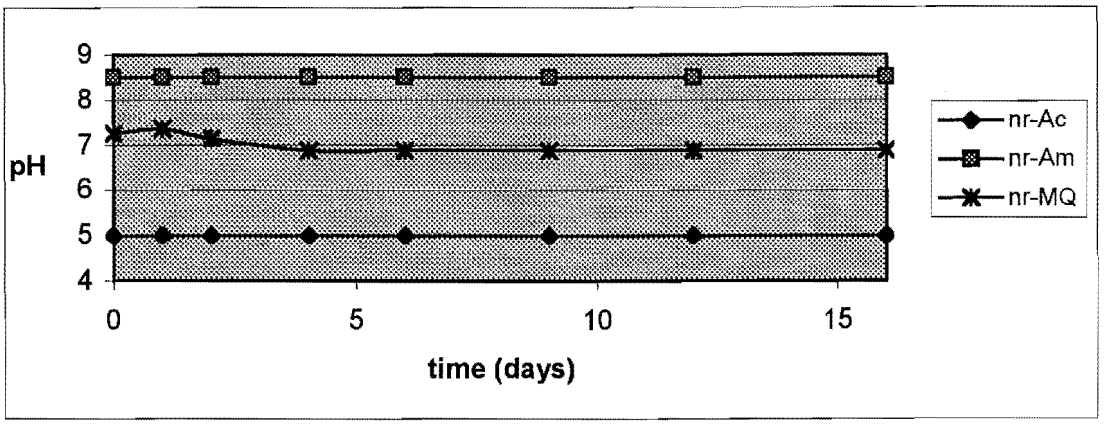
* Are results for the first leaching and, # results for leaching at day 16. The error for the lowest value (0.001 μg/g) is ± 0-10 % SD from the mean.

7.4.2.2 Oxic leaching

Leaching of GB 13 (oxic) was effected under non-recycled conditions, using Milli-Q water, acetate (pH 5.0) and ammonium (pH 8.5) buffers. The results are given in the following sections, for pH (Figure 7.9), As(V) and As(III) (Figure 7.10a-b), total Fe and E_h (Figures 7.11 and 7.12) and ASV-labile metals (Table 7.3).

a) pH

Figure 7.9: The pH of leachates from 65 g of GB 13 leached with non-recycled buffers and Milli-Q water under oxic conditions.



nr-Ac is non-recycled 0.1M acetate buffer at pH 4.7; nr-Am is non-recycled 0.1 M ammonium buffer at pH 8.5 and nr-MQ is non-recycled Milli-Q water.

b) As(V) and As(III)

For milli-Q water leachant, see the As(V) and As(III) results in method validation under reproducibility of leaching (Figures 7.2a-c).

Figure 7.10a: Arsenic leached from 65 g of GB 13 with non-recycled acetate buffer (pH 5) under oxic conditions.

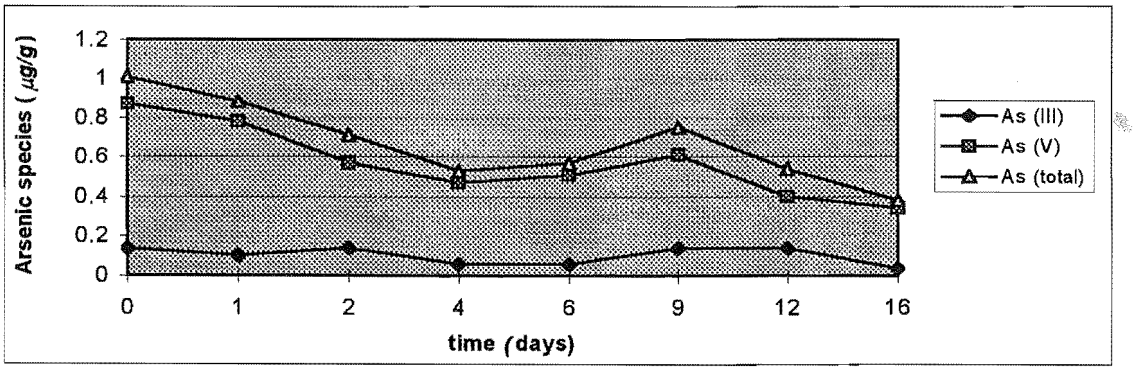
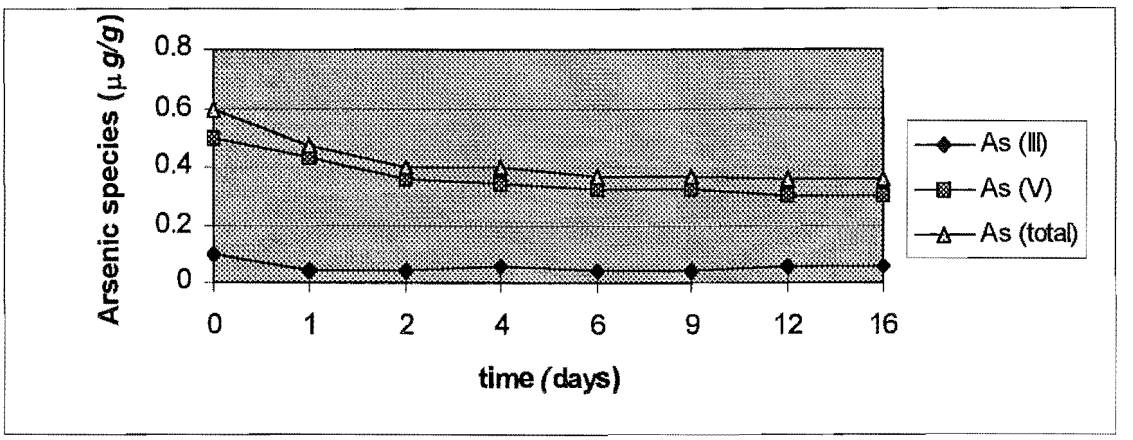
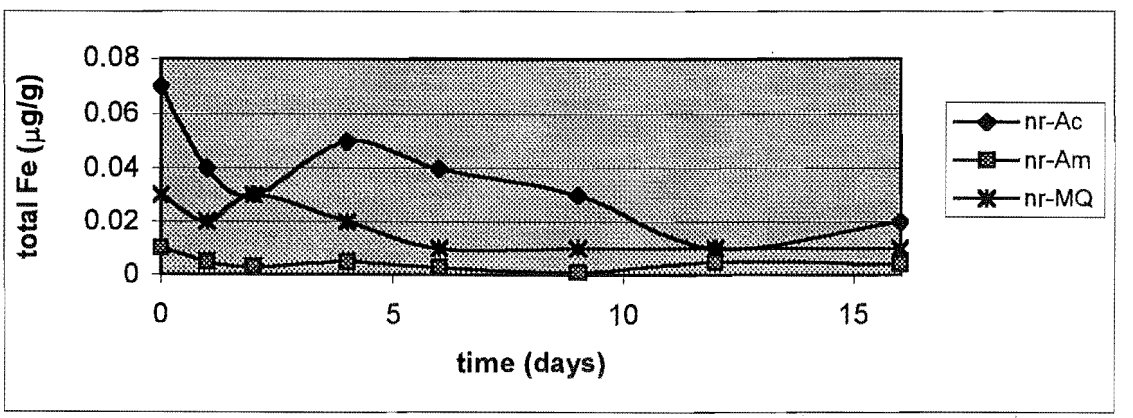


Figure 7.10b: Arsenic leached from 65 g of GB 13 with non-recycled ammonium buffer (pH 8.5) under oxic conditions.



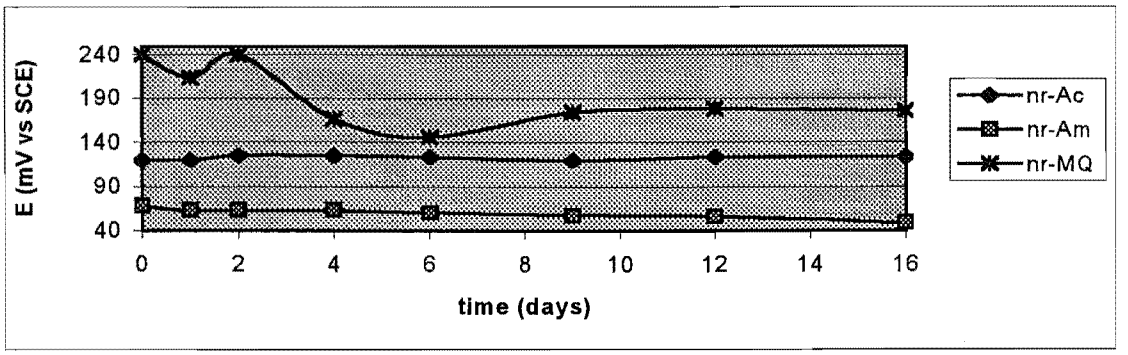
c) Fe and E

Figure 7.11. Total Fe leached from 65 g of GB 13 with non-recycled leachates under oxic conditions.



nr-Ac is non-recycled 0.1M acetate buffer at pH 4.7; nr-Am is non-recycled 0.1 M ammonium buffer at pH 8.5 and nr-MQ is non-recycled Milli-Q water.

Figure 7.12: The E in leachates from 65 g of GB 13 from non-recycled leachates under oxic conditions.



nr-Ac is non-recycled 0.1M acetate buffer at pH 4.7; nr-Am is non-recycled 0.1 M ammonium buffer at pH 8.5 and nr-MQ is non-recycled Milli-Q water.

d) ASV-labile metals

Table 7.3: ASV-labile metals leached from 65 g of GB 13 with non-recycled Milli-Q water, acetate and ammonium buffers under oxic conditions.

Leachate	Cu (μg/g)		Pb (μg/g)		Cd (μg/g)		Zn (μg/g)	
	0 d*	16 d #	0 d	16d	0 d	16 d	0 d	16 d
Milli-Q	0.002	0.001	0.003	0.001	0.002	0.001	0.003	0.001
Acetate	0.22	0.001	0.002	0.001	0.004	0.002	0.45	0.04
Ammonium	0.01	0.001	0.001	0.01	0.001	0.004	0.02	0.001

* are results for the first leaching and, # results for leaching at day 16. The error for the lowest value (0.001 μg/g) is ± 0-10 % SD from the mean.

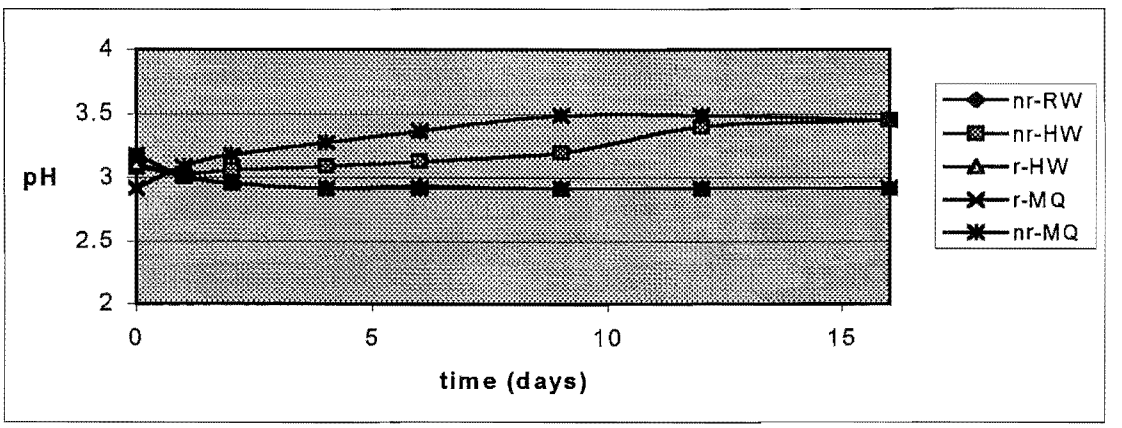
7.4.3 Acidic rock (Sandstone)

7.4.3.1 Anoxic leaching

Leaching of the sandstone was effected under cycled and non-recycled conditions, using Milli-Q water, rain water and humic water as leachants under anoxic conditions. The results are given in the following sections, for pH (Figure 7.13), As(V) and As(III) (Figure 7.14a-e), total Fe and E (Figures 7.15 and 7.16), ASV-labile metals (Figure 7.4) and conductivity 7.17.

a) pH

Figure 7.13: The pH of recycled and non-recycled leachates from 50 g of sandstone leached under anoxic conditions.



nr-HW is non-recycled rain water; nr-HW is non-recycled humic water; r-HW is recycled humic water, r-MQ is recycled Milli-Q water and nr-MQ is non-recycled Milli-Q water.

a) As(V) and As(III)

Figure 7.14a: Arsenic leached from 50 g of sandstone with non-recycled Milli-Q water under anoxic conditions.

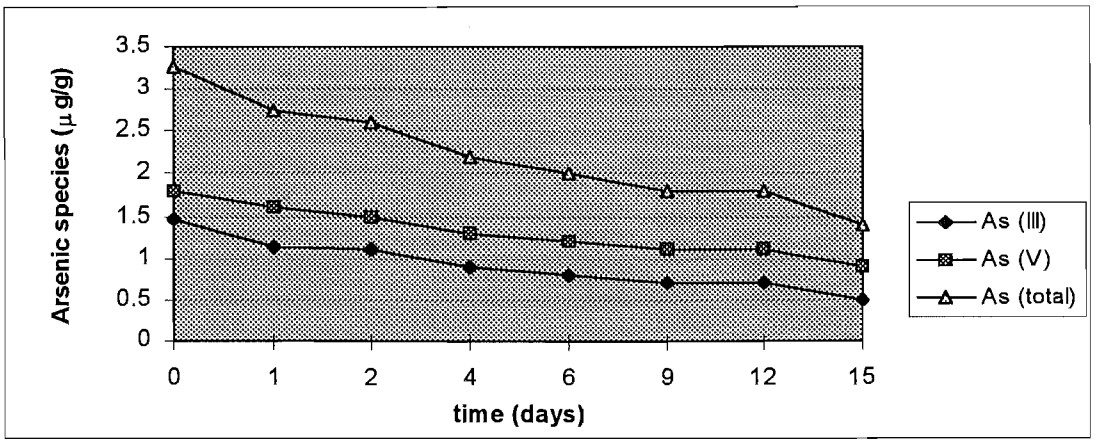


Figure 7.14b: Arsenic leached from 50 g of sandstone with recycled Milli-Q water under anoxic conditions.

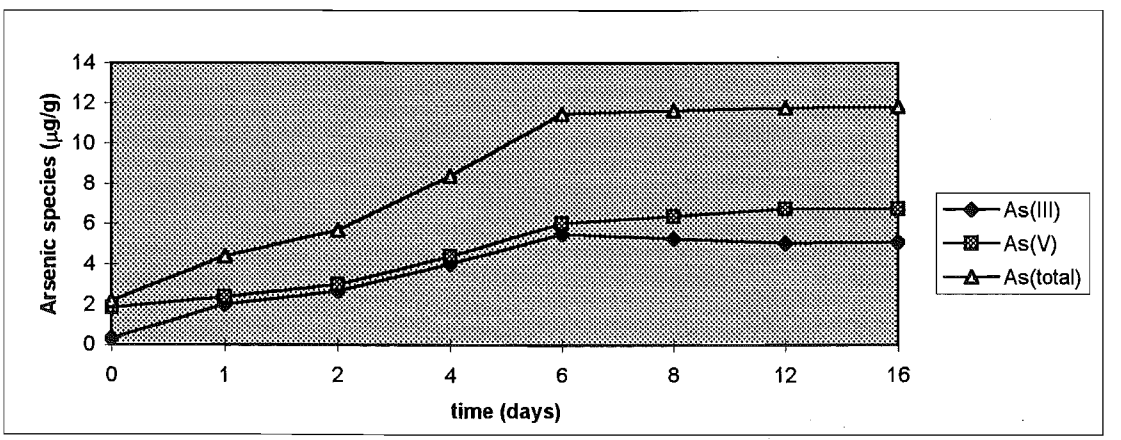


Figure 7.14c: Arsenic leached from 50 g of sandstone with non-recycled humic water under anoxic conditions.

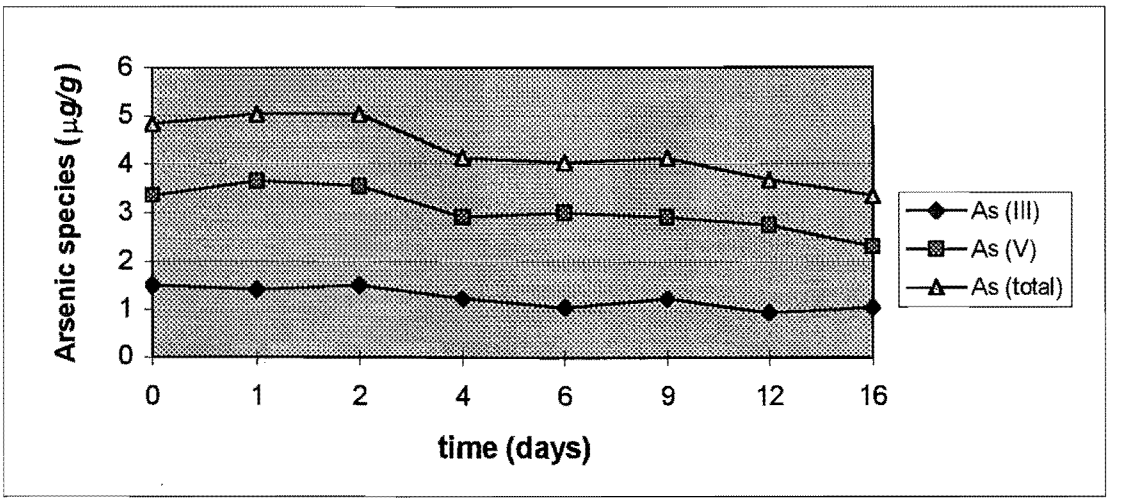


Figure 7.14d: Arsenic leached from 50 g of sandstone with recycled humic water under anoxic conditions.

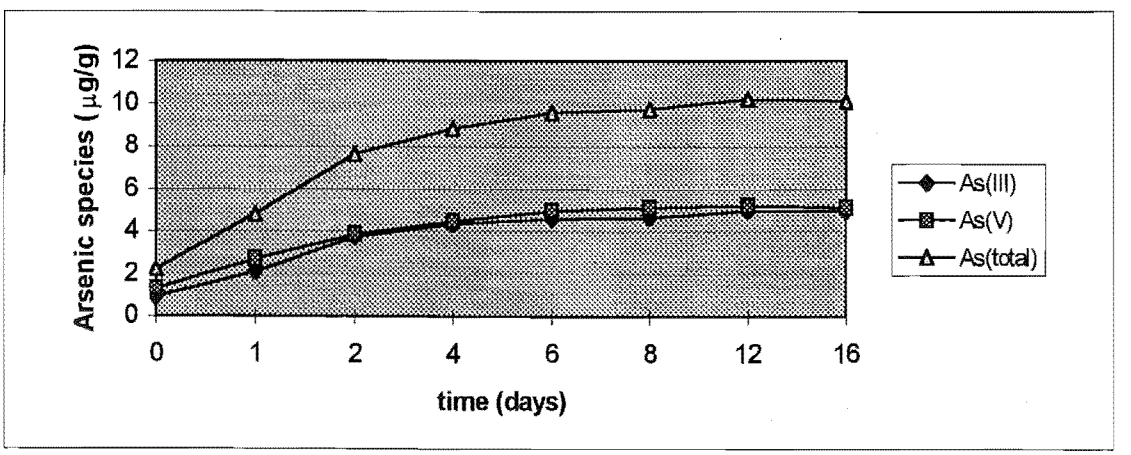
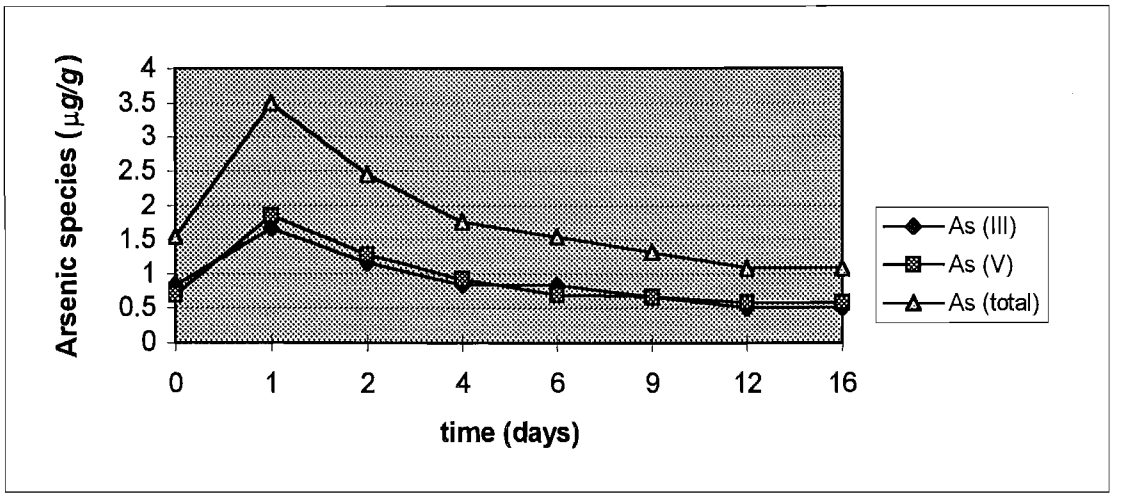
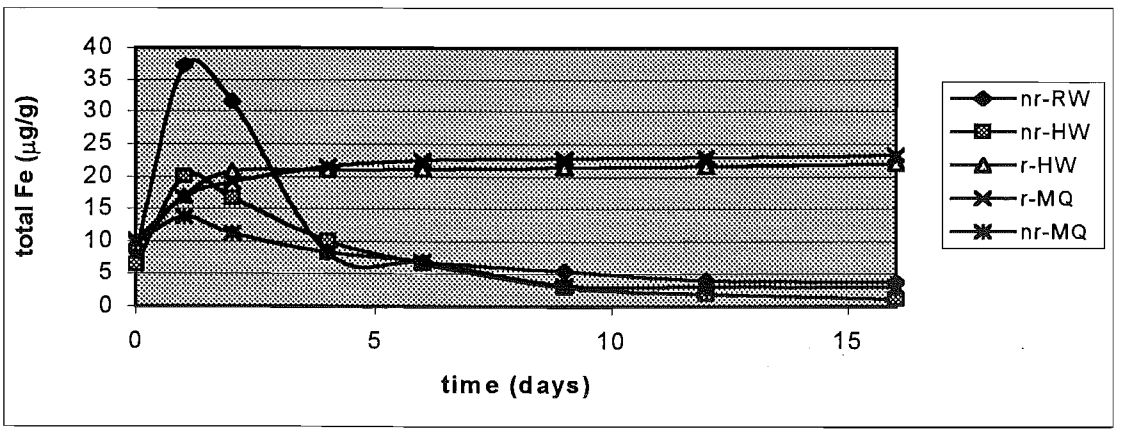


Figure 7.14e: Arsenic leached from 50 g of sandstone with non-recycled rain water under anoxic conditions.



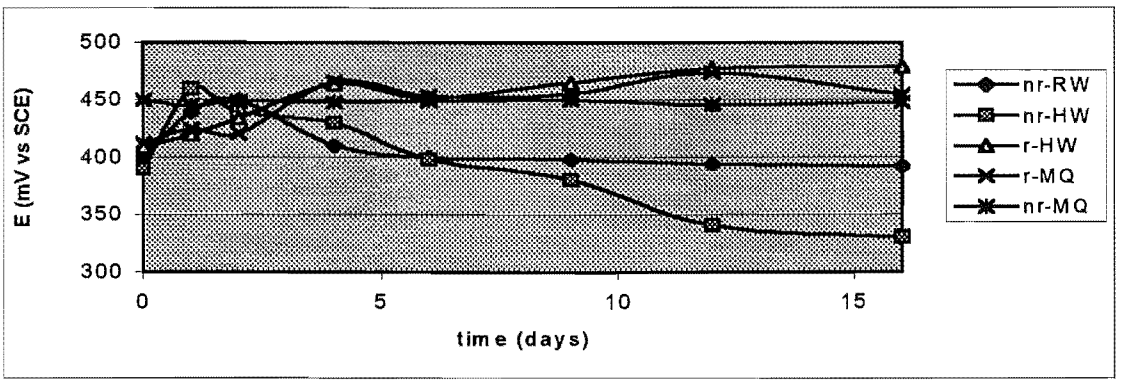
b) Total Fe and E

Figure 7.15: Total Fe leached from 50 g of sandstone with recycled and non-recycled leaching under anoxic conditions.



nr-HW is non-recycled rain water; nr-HW is non-recycled humic water; r-HW is recycled humic water, r-MQ is recycled Milli-Q water and nr-MQ is non-recycled Milli-Q water.

Figure 7.16: The E in leachates from 50 g of sandstone leached with recycled and non-recycled leachates under anoxic conditions.



nr-HW is non-recycled rain water; nr-HW is non-recycled humic water; r-HW is recycled humic water, r-MQ is recycled Milli-Q water and nr-MQ is non-recycled Milli-Q water.

c) ASV-Labile metals

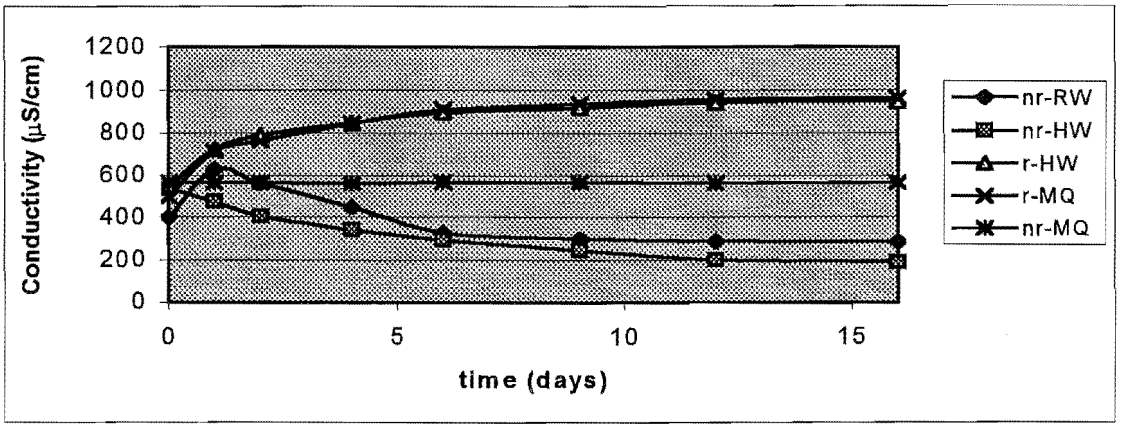
Table 7.4: ASV-labile metals leached from 50 g of sandstone with non-recycled leachates under anoxic conditions.

Leachate	Cu (μg/g)		Pb (μg/g)		Cd (μg/g)		Zn (μg/g)	
	0 d*	16 d#	0 d	16d	0 d	16 d	0 d	16 d
Milli-Q	0.05	0.02	0.18	0.02	0.002	0.0001	0.22	0.01
Rain	0.05	0.02	0.33	0.02	0.03	0.01	0.25	0.01
Humic	0.07	0.02	0.20	0.03	0.04	0.01	0.26	0.01

* are results for the first leaching and, # results for leaching at day 16. The error for the lowest value (0.001 μg/g) is ± 0-10 % SD from the mean.

d) Conductivity

Figure 7.17: The conductivity of leachates from 50 g of sandstone leached with recycled and non-recycled leachates under anoxic conditions.



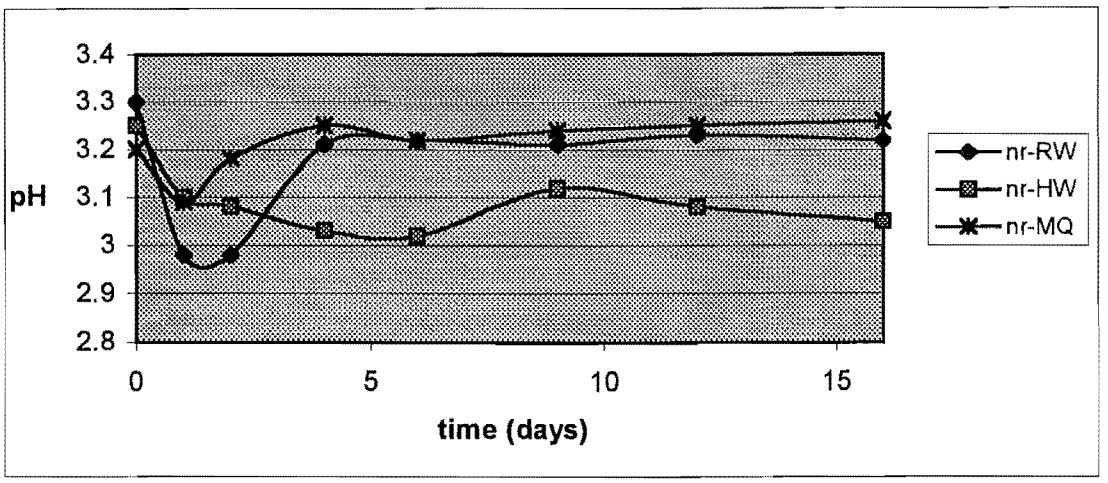
nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; r-HW is recycled humic water, r-MQ is recycled Milli-Q water and nr-MQ is non-recycled Milli-Q water.

7.4.3.2 Oxic leaching

Leaching of the sandstone was effected under non-recycled conditions, using Milli-Q water, rain water and humic water as leachants in contact with the atmosphere. The results are given in the following sections, for pH (Figure 7.18), As(V) and As(III) (Figures 7.19a-c), total Fe and E (Figures 7.20 and 7.21), conductivity (Figure 7.22) and ASV-labile metals (Table 7.5).

a) pH

Figure 7.18: The pH of non-recycled leachates from 50 g of sandstone leached under oxic conditions.



nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; and nr-MQ is non-recycled Milli-Q water.

b) As(V) and As(III)

Figure 7.19a: Arsenic leached from 50 g of sandstone with non-recycled Milli-Q water under oxic conditions.

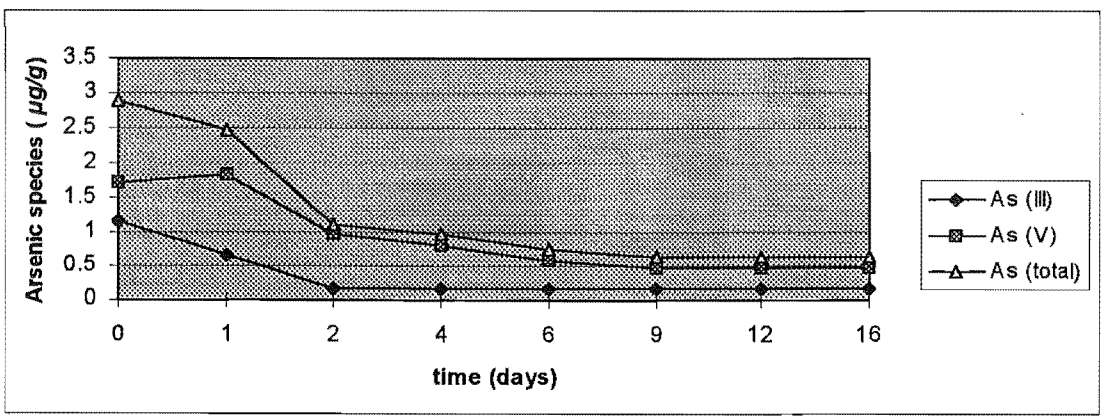


Figure 7.19b: Arsenic leached from 50 g of sandstone with non-recycled humic water under oxic conditions.

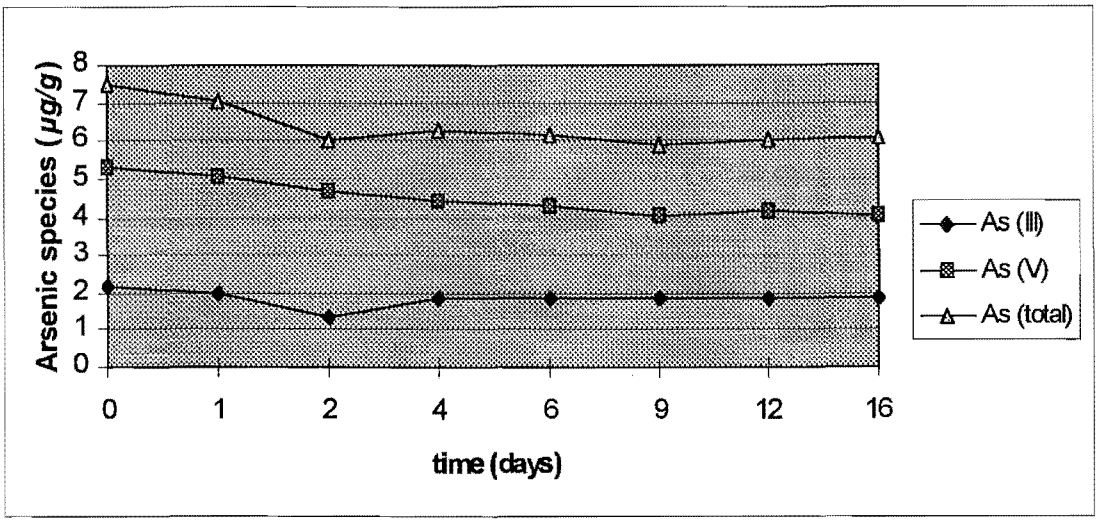
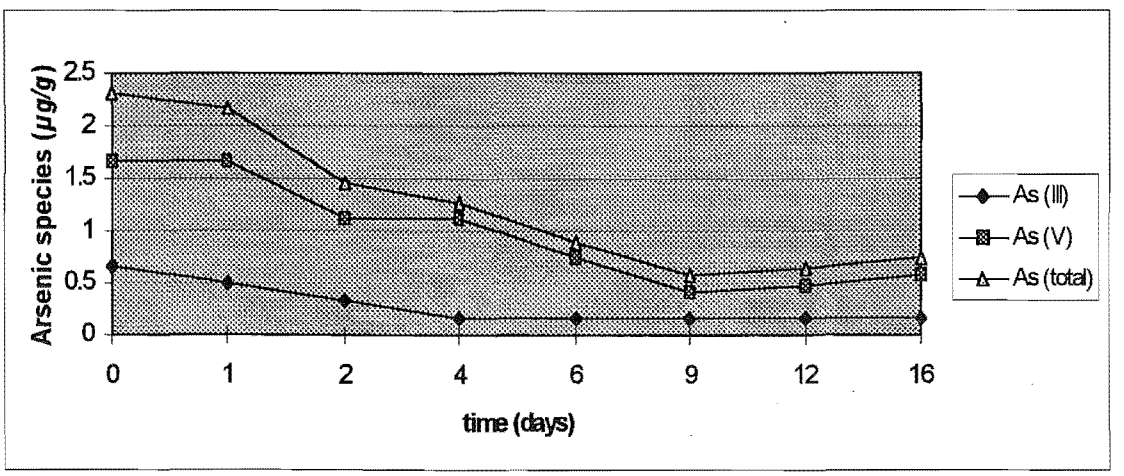
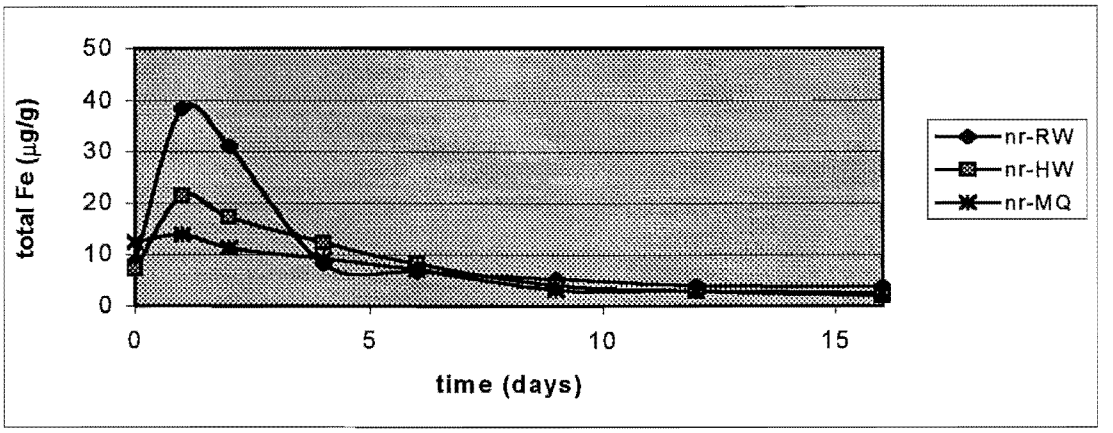


Figure 7.19c: Arsenic leached from 50 g of sandstone with non-recycled rain water under oxic conditions.



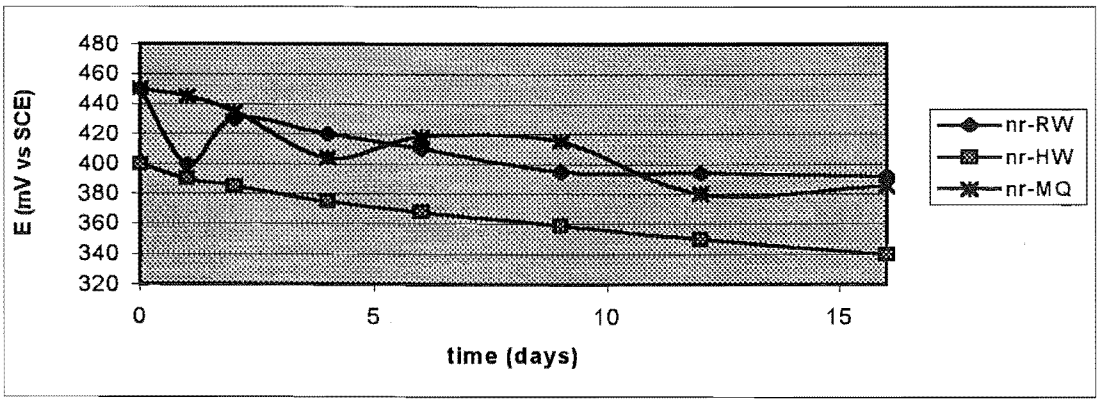
c) Fe and E

Figure 7.20: Total Fe leached from 50 g of sandstone with non-recycled rain, humic and Milli-Q water under oxic conditions.



nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; and nr-MQ is non-recycled Milli-Q water.

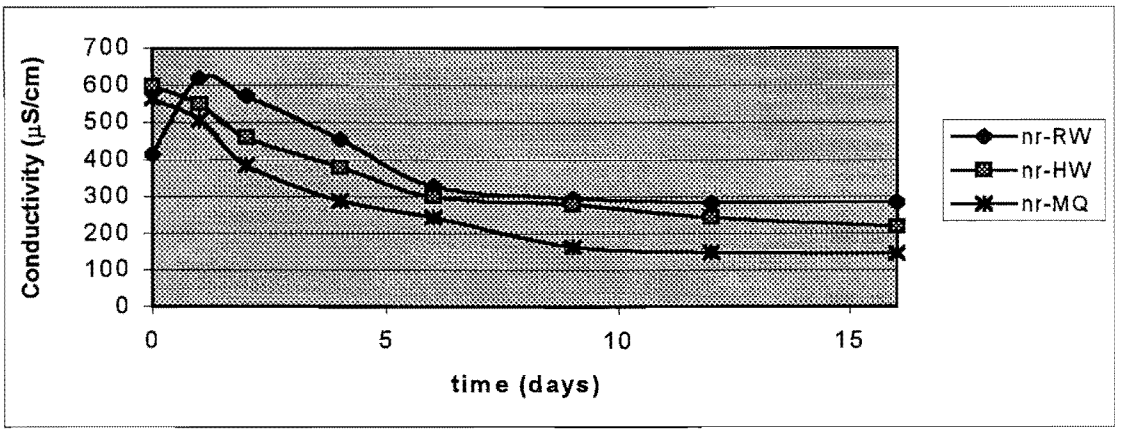
Figure 7.21: The E in leachates from 50 g of sandstone leached with non-recycled rain, humic and Milli-Q water under oxic conditions.



nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; and nr-MQ is non-recycled Milli-Q water.

d) Conductivity

Figure 7.22: The conductivity in leachates from 50 g of sandstone leached with non-recycled rain, humic and Milli-Q water under oxic conditions.



nr-RW is non-recycled rain water; nr-HW is non-recycled humic water; and nr-MQ is non-recycled Milli-Q water.

e) ASV-labile metals

Table 7.5: ASV-Labile metals leached from 50 g of sandstone with non-recycled rain, humic and Milli-Q water under oxic conditions.

Leachate	Cu (µg/g)		Pb (µg/g)		Cd (µg/g)		Zn (µg/g)	
	0 d*	16 d#	0 d	16d	0 d	16 d	0 d	16 d
Milli-Q	0.06	0.01	0.20	0.01	0.02	0.01	0.26	0.01
Rain	0.08	0.01	0.34	0.02	0.03	0.01	0.28	0.01
Humic	0.10	0.01	0.25	0.02	0.06	0.01	0.29	0.01

* are results for first the leaching and, # results for leaching at day 16. The error for the lowest value (0.001 µg/g) is ± 0-10 % SD from the mean.

7.5 DISCUSSION

7.5.1 Method validation

Method validation by way of leaching reproducibility showed that column-leaching methods applied in this work resulted in good reproducibility for pH, E and As(V)/As(III) measured. This is indicated by the results for arsenic (Figures 7.2a-c), total Fe (Figure 7.3) and those for pH, E and conductivity represented in Table 7.1. For example at day 0 (start of leaching) the mean concentrations for As(V), As(III) were 0.33 ± 0.02 μg/g and 0.30 ± 0.02 μg/g respectively. For total Fe (0.03 ± 0.01 μg/g) the % error was larger because of the lower measured value.

Another aspect investigated was the effect of sample storage on arsenic speciation. Results (Figure 7.4) showed that As(III) and As(V) concentrations from the sandstone leachate remained constant at ~3.4 and 4.2 μg/mL respectively. This showed that the speciation was not affected by prolonged storage at pH 2. It can therefore be inferred that leaching experiments and analytical measurements could be made reproducibly given that similar conditions were applied for each column leaching. In addition, the speciation of arsenic was not affected by the aging of leachates and hence samples could be stored for up to 14 days before a batch of samples was analysed for arsenic.

7.5.2 Acid generation

7.5.2.1 GB 13

a) Anoxic leaching

The pH of leachates from GB 13 (Figure 7.5) showed that the initial pH under both recycled and non-recycled leaching was weakly basic (~ pH 7.2). After 16 days of leaching, the pH increased upon recycled leaching but non-recycled leaching produced a weakly acidic pH of 6.7. This change in pH under non-recycled leaching of GB 13 presumably occurred in response to the depletion of ions or minerals that contribute to the

basicity of the rock sample. GB 13 is a carbonate bearing rock (see section 6.4.1.3) which gives rise to its high pH. The pH was not affected by the type of leaching solution (rain, humic or Milli-Q water).

b) Oxic leaching

Under oxic conditions, there was no change in pH with time when the rock was leached with acetate (5.0) and ammonium (8.5) buffer solutions (Figure 7.9). The pH of leachates from non-recycled Milli-Q water leaching did not differ from those for anoxic leaching in Figure 7.5. Thus the pH was not affected by the absence or presence of oxygen.

7.5.2.2 Sandstone

a) Anoxic leaching

Results for anoxic leaching of the sandstone waste rock shown in Figure 7.13 indicate that the pH is not strongly affected by the type of leaching solution used. The acid generation of the sandstone exceeds the buffer capacity of the leaching solutions. The pH was 2.9-3.4 when leached with recycled and non-recycled Milli-Q water. However, there was a slight increase from the initial pH of 3.0 to pH 3.4 after 16 days for non-recycled leaching with rain and humic water. This presumably occurred due to the depletion of ions or minerals that give rise to the acidity of the rock.

b) Oxic leaching

The pH values of non-recycled Milli-Q, rain and humic water (Figure 7.18) indicated highly acidic leachates (~ pH 3.1-3.3) following 16 days of leaching. The Milli-Q, rain and humic water leachates exhibited similar acidic pH. These results indicate that the leaching solution used did not buffer the acidity generated by the sandstone.

The pH was consistent with that reported in section 6.4.2.2 for batch leaching of the sandstone. The initial pH for each leachate (t = 0) was 2.9-3.2 (anoxic) and 3.2-3.3 (oxic). These results were similar to pH measured (3.3-3.4) for batch sandstone leaching in section 6.4.2.2.

7.5.3 Arsenic

7.5.3.1 GB 13

a) Anoxic leaching

The results in Figures 7.6a-e are for As(V) and As(III) species leached from the GB 13 waste rock under anoxic conditions. The results show that As(V) is the dominant species in all leachates. This is consistent with the E-pH measurements (Table 7.1), which indicate that As(III) is not thermodynamically favoured (Figure 1.1).

For both recycled and non-recycled leaching arsenic concentrations were in the order of humic > rain > Milli-Q water. For example, following 16 days of non-recycled leaching, As(V) concentrations leached from GB 13 by humic, rain and Milli-Q water were 0.6, 0.4 and 0.1 μg/g respectively. The recycled leachates accumulate arsenic species over the duration of leaching. This accumulation is demonstrated by the recycled humic water (Figure 7.6d) which show increases of 2.25 μg/g (As(V)) and 0.58 μg/g (As(III)) from day 0 to day 16 of the leaching process.

b) Oxic leaching

The concentrations of As(total) for GB 13 which were leached by the 0.01M acetate buffer (Figure 7.10a) were 2 fold higher than that leached by the ammonium buffer (Figure 7.10b) and Milli-Q water. This can be attributed to the acidity of the acetate (pH 5.0) which increases the rate of dissolution of arsenic from the waste rock.

7.5.3.2 Sandstone

a) Anoxic leaching

Figures 7.14a-e show the results for the arsenic species leached from the sandstone under anoxic conditions. The dominant arsenic species is As(V), as for the GB 13. This again is consistent with E-pH values measured. Following 16 days the arsenic species measured

showed concentrations in the order of humic > Milli-Q > rain water (non-recycled leaching). However for recycled leaching arsenic concentrations were in the order of Milli-Q > humic > rain water. Under recycled leaching the amount of each arsenic species and hence total arsenic is accumulated through the duration of leaching.

Batch leaching (section 6.4.2.2) of the sandstone at day 3 produced 4.2 μg/g of As(V) and 3.0 μg/g of As(III) under strictly anoxic conditions. In this work recycled humic leaching gave rise to 4.2 μg/g of As(V) and 4.0 μg/g of As(III), whereas recycled Milli-Q water leached 6.0 μg/g As(V) and 5 μg/g of As(III) after 16 days.

b) Oxic leaching

The total arsenic concentrations (Figures 7.19a-c) measured following 16 days of non-recycled leaching were in the order of humic > Milli-Q > rain water. As(V) was the dominant arsenic species. For humic water leaching under oxic conditions a higher concentration of total arsenic was leached than under anoxic conditions. The humic water leaching showed that at 16 days 6 μg/g As was leached compared to 4.8 μg/g As under anoxic conditions. However, for non-recycled Milli-Q and rain water the total arsenic leached under oxic was lower than anoxic conditions.

In section 6.4.2.2 (batch leaching) the As(V) and As(III) leached from the sandstone were 10.1 μg/g and 8.2 respectively. These concentrations were higher due to constant contact of the leachant with the sample and because oxygen was bubbled through the leachant increasing the dissolution rate of the As(V) and As(III) from FeAsS.

7.5.4 Fe and E

Analyses of leachates indicated the absence of colloids and hence there are no data for colloidal Fe.

7.5.4.1 GB 13

a) Anoxic

The concentrations of soluble Fe leached by rain, Milli-Q and humic waters decreased to <0.01 μg/g at 16 days under non-recycled leaching, as shown in Figure 7.7. This indicates that soluble Fe is depleted over the duration of leaching. The Figure shows that under recycled leaching slightly more Fe is leached (0.06 μg/g) by the humic water compared to Milli-Q, which leached 0.04 μg/g at 16 days. Presumably, the humic water facilitates dissolution of FeAsS and FeS_2 through the binding of Fe.

b) Oxic

Figures 7.11 and 7.12 show results for soluble Fe and E respectively. Fe results in Figure 7.11 indicate that an acidic leachant (acetate buffer) leaches more Fe than a basic leachant (ammonia buffer). Therefore this implies that the amount of Fe leached would depend on the acidity of the leachant. The Fe concentrations corresponded to differences in the E measurements, which show that the E is higher (180 mV vs. SCE at 16 days) for acetate buffer and for the basic leachant (120 mV vs. SCE at 16 days).

After 16 days of both non-recycled and recycled leaching (all leaching solutions) the E values for GB 13 were ~160 to 200 mV vs. SCE (Figure 7.8). The E in conjunction with the pH results obtained for both rock types are consistent with an oxidising environment. Under these conditions AsO_4^{3-} is the more stable As species.

7.5.4.2 Sandstone

a) Anoxic

Results in Figure 7.15 indicate that the Fe concentration leached from the sandstone was higher than that leached from GB 13. Non-recycled leaching using Milli-Q, rain and humic water resulted in a steady decrease in soluble Fe leached during the course of the leaching (e.g. <5 μg/g at 16 days for all leaching solutions). The different leaching solutions led to no significant differences in the soluble Fe leached under non-recycled

leaching. In contrast recycled Milli-Q and humic water leached ~ 22 and 24 μg/g respectively. These values are cumulative because of leachant recycling. These results also suggest that under recycled leaching the Fe concentrations do not vary with type of leachant.

In section 6.4.2.2 (batch leaching) the total Fe leached from the sandstone was ~55 μg/g. This concentration is much higher and again is due to constant contact of the leachant with the sample.

The E values measured for the system (Figure 7.16) are assumed to reflect the ratio of Fe(III):Fe(II) in each solution. The measured value for Milli-Q water (*ca.* 450 mV vs. SCE) corresponds to 690 mV vs. SHE and is close to the value of 750 mV vs. SHE calculated from the measured Fe(III) and Fe(II) concentrations in the batch leaching experiments of Chapter 6 (see section 6.4.2.1). Thus it can be assumed that it is the Fe(III):Fe(II) ratio that is controlling E and therefore the E_h.

Figure 7.16 also shows that, with time, E values of non-recycled leachates are lower than those of the corresponding recycled leachates. This implies that the ratio of Fe(III):Fe(II) is lower for non-recycled leachates. Figure 7.13 shows that the pH of the non-recycled leachates is higher than that of the corresponding recycled leachates (pH 3.45 and 2.95 respectively).

b) Oxic

The results for soluble Fe shown in Figure 7.20 are similar to those obtained by anoxic leaching with non-recycled leaching by rain, humic and Milli-Q waters. At 16 days the amount of soluble Fe leached was <5 μg/g for all leachates. Therefore, the leaching environment (anoxic/oxic) did not affect the rate of Fe dissolution from the waste rock.

In section 6.4.2.2 (batch leaching) the total Fe leached from the sandstone was 142 μg/g. This concentration is much higher for batch leaching due to constant contact of the leachant with the sample. Further, oxygen was bubbled through the leachant thus creating

a vigorously oxic condition and therefore increasing the dissolution rate of Fe from the rock.

The E values at 16 days were 340, 385 and 390 mV vs. SCE for humic, Milli-Q and rain water respectively. These values were lower than the initial (day 0) measurements; 400 mV vs. SCE for humic water and 450 mV vs. SCE for both rain and Milli-Q water.

7.5.5 Heavy metals

GB 13 and Sandstone

The data in Tables 7.2 (GB 13-anoxic), 7.3 (GB 13 oxic), 7.4 (sandstone-anoxic) and 7.5 (sandstone-oxic) indicate that leachates from the sandstone contain concentrations of leachable ASV- labile metals which are much higher than those from GB 13 waste rock. This results from increased leachate acidity from the sandstone. Acidity increases waste rock dissolution and this was confirmed by the leaching of GB 13 with acetate (pH 5) and ammonium (pH 8.5) buffers. The acetate buffer leached more heavy metals than the ammonium buffer. For each metal the amount leached was not affected by the type of leachant nor the leaching conditions (anoxic/oxic). Overall, the leachant concentrations were similar to those in a polluted fresh water system (Batley and Florence, 1980).

7.5.6 Conductivity

Conductivity (Figures 7.17 and 7.22) decreases when leachates are not recycled but increases on recycling of leachates. Overall, the conductivity from sandstone leaching is much higher than GB 13 (Table 7.1). This suggest that higher conductivity (ionic strength) leachates would initially occur from a waste rock stack, but then gradually decline to natural levels over a duration of time. The type of leachants did not significantly alter the conductivity measurements.

7.5.7 Recycled verses non-recycled leaching

There are examples in this work where As and Fe from a recycled or non-recycled leaching reach a plateau. Examples of this can be see in Figures 7.6a, 7.6b, 7.14a, 7.14b, 7.15, 7.19a and 7.20. Under recycled leaching the results are expected to be additive, however this did not occur. This suggests that under recycled leaching a layer ($Fe(OH)_3$) forms on the surface of the rock which prevents further dissolution. Under non-recycled leaching the rock is subjected to fresh leachant (as would occur at the top of a waste rock stack exposed to rain water or elsewhere in the stack where humic water seeps from surroundings).

The apparatus used for non-recycled leaching did not entirely maintain an anoxic environment since the N_2 atmosphere was interrupted on each addition of leachant. This may explain why there were instances where results of anoxic verses oxic were similar (compare Figures 7.15 and 7.20, 7.17 and 7.22).

7.6 CONCLUSION

The rock which has the greatest potential to produce acid mine drainage (AMD) is the sandstone waste rock. Its leachates give a high acidity of pH 2.9-3.4 compared to leachates of the GB 13 waste rock which have a weakly basic pH of 7.2. Further the sample keeps on producing AMD at day 16 which means that in the field situation the sandstone would continue to produce acidity after 4 years of rainfall. The pH is not affected by the type of leaching solution used (rain, humic or Milli-Q water). The higher the acidity the greater the rate of dissolution of FeS_2 and FeAsS resulting in an increase in arsenic, Fe and ASV-labile metal concentrations. This was demonstrated by dissolution of GB 13 with the weakly acidic acetate buffer (pH 5) compared to weakly basic ammonium buffer (pH 8.5).

The dominant arsenic species in leachates of both rock samples is As(V). This is consistent with measured E-pH. The concentrations of arsenic leached from the sandstone were greater than those leached from GB 13. There was no significant effect on the rate of leaching for each waste rock when different types of leachants were used for leaching.

The soluble Fe and heavy metals were higher for the leachates of sandstone than GB 13. The Fe levels appear to control the measured value of E and this is supported by calculations for the Fe(II)/Fe(III) redox couple, as given in section 6.4.2.1. The concentrations of heavy metals (Cu, Cd, Pb, and Zn) would be reduced when discharged into a fresh water catchment due to processes of dilution, complexation to dissolved organics and adsorption onto sediments.

The implications of this work for a waste rock stack is that the upper layer (oxic) will tend to be depleted faster of its AMD components through percolation of rainfall. As the leachate percolates further down to the lower regions of the stack it becomes anoxic in nature. At this stage it becomes saturated with AMD components such as Fe, sulfate and As(III) and As(V). There is some coating of rock surfaces with $Fe(OH)_3$, thus passivating the leaching process. This coating will adsorb some of the arsenic from the leachate.

CHAPTER 8

CONTROL OF ARSENIC IN LEACHATES

This Chapter reports the use of limestone for the control of arsenic in mine waste rock leachates. It also establishes which element in the limestone is responsible for the oxidation of arsenite and the removal of arsenic species.

8.1 INTRODUCTION

The control of waste rock acidity has been the main thrust in most of the work published to date. In contrast, this work concerns the capture of As released from oxidation of FeAsS. Arsenopyrite is a minor component of FeS_2 and the amount of As produced is significantly less than the acid produced.

Work presented in Chapter 5 established that AsO_4^{3-} forms a number of insoluble products and is strongly adsorbed to FeO(OH)(s). It also established that As(III) forms products that are more soluble, that it is less strongly adsorbed to FeO(OH)(s) and that it can be readily oxidised to As(V) in the presence of FeO(OH)(s). Experimental results from the Chelex-Fe(III) work (Chapter 3) showed that As(III) is oxidised on contact with precipitated FeO(OH)(s) in the resin.

This Chapter describes the control of As(V) concentration in leachates by precipitation of Fe(III) (as FeO(OH)) which is present in excess over As. The precipitation is achieved by buffering with limestone. It also investigates the As(III) oxidation by Fe(III) in solution and its oxidation and uptake by FeO(OH)(s). Further, it investigates whether Fe(III) and/or Ca in limestone are responsible for the uptake of both arsenic species.

8.1.1 Literature review

The mineral processing industry for many years has practiced the removal of arsenic from process solutions and effluents. The various separation methods include oxidation-reduction, precipitation, adsorption, electrolysis, solvent extraction, ion exchange, membrane separation, precipitate flotation, ion flotation and biological processes (Robins, 1983a).

Formation of insoluble arsenic compounds has been used for the removal of arsenic from aqueous systems. The most common practice in treatment processes is the oxidation of As(III) to As(V) then its removal from solution by the formation of ferric or calcium arsenates. Removal from solution as calcium arsenate is through precipitation with lime (Robins, 1983a). Calcium can precipitate both arsenite and arsenate but the solubility of arsenites is greater than arsenates. Further, atmospheric carbon dioxide will decompose calcium arsenates above pH 8.3 to calcium carbonate (Robins, 1983a, Robins, 1983b). It has been found that lime is effective short term at pH > 12 and it is possible to reduce the arsenic concentration to less than 1 mg/L, but the precipitates of $Ca_3(AsO_4)_2$ and $Ca_3(AsO_4)_2.H_2O$ which are formed in this pH region decompose to $CaCO_3$ in the natural environment.

The solubility and stability regions for calcium arsenites and arsenates in aqueous solutions at 25 °C have been evaluated by Nishimura and Robins (1998). This was done by studying the systems Ca(II)-As(III)-H_2O and Ca(II)-As(V)-H_2O, by equilibrating mixtures of calcium oxide with As(III) and As(V) solutions (pH > 8) in the absence of carbon dioxide for one month. Chemical analysis was done on solids and associated solutions. X-ray diffraction analysis indicated the existence of $Ca(AsO_2)_2$ and $CaAsO_2OH.1/2H_2O$ in the system Ca(II)-As(III)-H_2O. It indicated $Ca(H_2AsO_4)_2$, $CaHAsO_4.H_2O$, $Ca_3(AsO_4)_2.4H_2O$ and $Ca_2AsO_4OH.2H_2O$ in the system Ca(II)-As(V)-H_2O. The solubility and stability regions for these compounds were assessed as a function of pH. Another compound which forms at pH > 8 is $Ca_{10}(AsO_4)_6(OH)_2$(s) Mahapatra *et al.* (1987). Further discussion devoted to the role of calcite ($CaCO_3$) is given in section 1.3.2.

Skousen *et al* (1997) researched AMD treatment with limestone and found that the effectiveness of limestone is reduced by 10% by armouring (formation of insoluble FeO(OH)(s)) on the limestone surface). Inskeep *et al.* (1997) established that use of lime could immobilise arsenic in mine tailings.

Arsenite is the more toxic arsenic species and therefore its control by oxidation to the less toxic As(V) should be part of any process for removal of arsenic from mine leachates.

8.2 SCOPE OF THIS WORK

This work was concerned with (a) controlling the arsenic concentration in leachates from mine waste rock by formation of FeO(OH) through buffering with limestone and (b) establishing the centers or element(s) in the limestone responsible for retention of As(III) and As(V), and the oxidation of As(III) during the treatment of leachates. This involved:

i) Studying arsenic removal from leachates by generation of ferric hydroxide precipitates. The formation of FeO(OH)(s) precipitates was achieved by buffering of synthetic leachates by passing them over limestone.

   The concentrations of Fe(III) and As used in this work mimicked the quantities that can arise from sandstone leachates, which contain Fe (20 ppm) far in excess of total As (2 ppm). To simulate the role of individual components of the sandstone leachates, synthetic solutions were used that contained one or more of Fe/As/sulfate at concentrations similar to those in sandstone leachate.

ii) Conducting experiments to study the subsidiary role of the limestone in the removal of As, i.e. limestone chemistry other than precipitation of FeO(OH). In particular, the formation of insoluble Ca arsenates and the interaction of As(V) with Fe impurities in the limestone were studied.

8.3 EXPERIMENTAL

The limestone used in all column leaching was from Mt. Somers. This was sieved to 1-10 mm diameter. The columns used were those for waste rock leaching, described in section 7.3.1.

8.3.1 Waste rock leachates and limestone layers

To investigate the effects of limestone layered with waste rock, experiments were conducted in which non-recycled milli-Q water (60 mL) was added at specific time intervals to columns containing limestone and the sandstone waste rock. The amount of sandstone was 65 g with the layers each containing 10 g of limestone. This was conducted under oxic conditions. The placement of limestone layers in the columns containing the sandstone were as follows:

i) cap
ii) base
iii) cap and base.

For these experiments 2 mL aliquots of leachate were taken and 0.025 μm membrane filtered, acidified to pH 2 (HCl – BDH Aristar) and stored. The As(V) and As(III) were analysed using the modified molybdenum blue spectrophotometric method described in section 2.3.11. Total Fe in the leachates was measured using the flame atomic absorption method given in section 2.3.5. Other parameters such as pH and E were measured by the methods given in sections 2.3.1.2 and 2.3.1.4 respectively.

8.3.2 Kinetic leaching tests on limestone using synthetic solutions

The removal of As(V) from synthetic solutions was studied through recycled leaching tests. Solutions at pH 3.0 were prepared to mimic As(III), As(V) and Fe(III) concentrations in sandstone leachates. In each run 30 mL of the synthetic solution was recycled through the column containing 30 g of limestone. Tests were conducted by passing the following solutions through the limestone.

i) 5 ppm As(V)
ii) 5 ppm As(V) and 20 ppm Fe(III)

iii) 5 ppm As(V) and 200 ppm sulfate

iv) 5 ppm As(V), 20 ppm Fe and 200 ppm sulfate.

For these experiments, 0.5 mL aliquots were taken at intervals throughout the duration of leaching, 0.025 μm membrane filtered and acidified to pH 2.0 (HCl – BDH Aristar). The filtrates were stored and the As(V) analysed using the hydride generation method given in section 2.3.4. Fe was measured using the GFAAS method given in section 2.3.3.

To study the effect of limestone on As(III) in leachates the following experiments were conducted:

i) A 1 ppm As(III) solution (30 mL) was recycled over 30 g of limestone until a total of 360 mL had passed through the column.

ii) A second solution containing 1 ppm As(III) and 20 ppm Fe(III) (30 mL) was recycled over a fresh 30 g of limestone for a similar period. Aliquots (0.5 mL) were taken, filtered (0.025 μm) and analyzed for As(III).

iii) Solutions containing 1 ppm As(III) were made up in 1 L of limestone-equilibrated water and left standing for 4 days. Aliquots (1 mL) were taken at various intervals, membrane filtered (0.025 μm) then analyzed for As(III).

iv) Solutions (1 L) containing 1 ppm As(III), 800 ppm Ca as calcium chloride plus calcium carbonate were left to stand for 3 days. Aliquots (1 mL) were taken at various intervals, membrane filtered (0.025 μm) and analyzed for As(III).

To investigate As(III) oxidation by Fe(III) the following experiments were conducted:

i) A 250 mL solution containing 5 ppm As(III) and 40 ppm Fe(III) at pH 3 was allowed to react for 14 days. Aliquots (1 mL) were taken at intervals, membrane filtered (0.025 μm) and analyzed for As(III).

ii) Two separate 100 mL solutions containing As(III) were recycled over 30 g of limestone in separate columns, the first for 1 hr and second for 24 hr. Leachates were sampled after 1 hr and 24 hr respectively. At the completion of the experiments the limestone was washed with 0.1 M HCl (BDH-Aristar) and the acid analysed for both As(III) and As(V).

All 0.025 μm membrane filtered aliquots from the As(III) leaching experiments were acidified to pH 2.0, made up to 50 mL with milli-Q water then the As(V), As(III) and as appropriate Fe content measured. The pH in each case was measured before acidification of the fractions. The As(V) and As(III) were measured using the hydride generation technique described in section 2.3.4 whereas total Fe was measured by GFAAS as described in section 2.3.3.

8.3.3 The role of Fe impurities in the limestone

In addition to the buffering properties of limestone it was assumed that Fe impurities could play a role in adsorbing As(V) and catalysing the oxidation of As(III). These assumptions were the basis of the following experiments.

8.3.3.1 Solid state properties

The Fe content of limestone was determined by XRF. The oxidation state and crystallographic environment of Fe centres were determined by Mossbauer spectroscopy. Details of the XRF and Mossbauer facilities are described in Chapter 2.

8.3.3.2 Reactive sites on the limestone surface

The following experiments were conducted to probe the role of Fe impurities in the adsorption of As(III) and As(V) on the limestone surface:

i) Limestone (30 g) was pre-washed with milli Q water until all loose particulates were removed. Then a 250 mL solution containing 5 % ascorbic acid, 10^{-4} M phenanthroline and 0.1 M acetate buffer (pH 5.0) was passed (~1 mL/min) over the limestone layer allowing for adequate contact time. Then 100 mL solutions containing 5 ppm As(V) and 1 ppm As(III) were recycled over the pre-treated limestone using separate columns for each species. Aliquots (0.5 mL) were taken at regular intervals, filtered (0.025 μm) and analysed for As(III) and As(V).

ii) Dilute sulfuric acid (0.001M) was passed over 30 g of fresh limestone. This was to mimic acid mine drainage induced surface renewal of the limestone. Samples were taken, membrane filtered (0.025 μm) and the total Fe was measured by GFAAS.

8.3.3.3 Precipitation of calcium arsenate

To determine if Ca dissolved from the limestone surface was responsible for arsenic removal, 100 mL solutions containing 1000 ppm Ca^{2+} and 5 ppm As(V) were prepared in Milli-Q water at pH 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0. The pH was controlled by adding appropriate amounts of concentrated HCl (BDH-Analar). These solutions and were left for 20 days at room temperature under N_2 flushing. After 20 days (when solution equilibration was assumed), the solutions were membrane filtered (0.025 μm) and the As(V) measured.

For experiments 8.3.3.2-8.3.3.3, all 0.025 μm membrane filtered aliquots were acidified to pH 2.0, made up to 50 mL with Milli-Q water then the As and/or Fe content measured. The As(V) and As(III) were measured using the hydride generation technique described in section 2.3.4 whereas total Fe was measured by GFAAS with the instrument described in section 2.3.3.

8.3.4 Acid neutralisation potential of the basic waste rock GB 13

The acid neutralisation capacity of the basic waste rock (GB 13) and the ratio of GB 13 to acidic sandstone in the mine waste indicates that GB 13 has sufficient capacity to neutralise acid leachates from the sandstone. However this capacity would be realised only if its rate of weathering is sufficiently fast. This kinetic aspect was investigated. This was done by passing (daily) non-recycled milli Q water (30 mL) over 30 g of GB 13 on top of a 1 g sandstone layer for a duration of 12 days. The eluant pH was monitored over the course of leaching. The ratio of sandstone (acidic) to GB 13 (weakly alkaline) was obtained from Macraes Mining data (Macraes Mining Company Ltd, 1994) and was consistent with the average composition of the waste rock at the proposed mining site.

8.4 RESULTS AND DISCUSSION

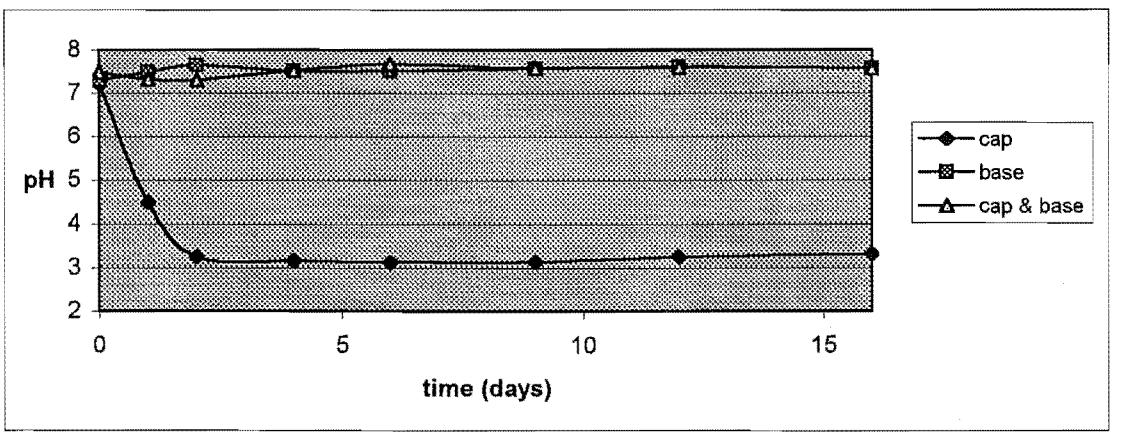
8.4.1 Column leaching

8.4.1.1 Leaching of sandstone with limestone layers

The sandstone waste rock with limestone layers placed at the cap and or base was leached under oxic conditions with non-recycled Milli-Q water. The results for pH, As(V), As(III), total Fe and ASV-labile metals are given below.

a) pH

Figure 8.1. The pH of leachates from the non-recycled Milli-Q water leaching of the sandstone waste rock (50 g). Limestone layers (10 g) were placed at the cap, base or cap and base.



The pH of the sandstone leachate leached with recycled Milli-Q water was ~3.4 following 16 days of leaching. The result for this is given in Figure 7.13 (Chapter 7). The inclusion of limestone layers affected the pH of the resultant leachates as shown in Figure 8.1. The observed pH related to where the layer of limestone was placed in the leaching column. After 16 days the pH was strongly acidic when the limestone was placed as a capping layer over the sandstone but was weakly basic when the layer was placed at the base or base plus cap.

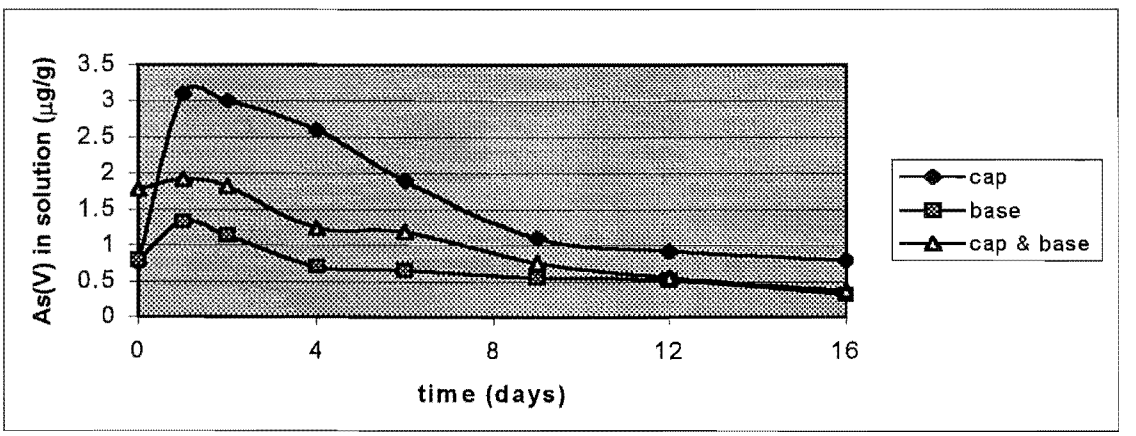
From this it can be inferred that the rate of dissolution of limestone in water and production of alkalinity is less than the rate of production of acid by leaching of sandstone

(limestone cap). In contrast, the rate of reaction of limestone with acid matches the rate of acid production from leaching of sandstone (limestone cap/cap and base).

b) Arsenic

Measurements for the limestone layer experiments (Figure 8.2) showed that only As(V) was detectable in the final leachates. Further, inclusion of the limestone layers at the base of the columns had a marked effect on the amount of arsenic leached. This is when compared with arsenic results for non-recycled Milli-Q water leaching of the sandstone as shown in Figure 7.14a (Chapter 7).

Figure 8.2. Concentrations of arsenic species in leachates from the non-recycled Milli-Q water leaching of sandstone waste rock (50 g). Limestone layers (10 g) were placed at the cap, base, or cap and base.



After 16 days, leaching with a limestone cap or cap and base, the concentration of As(V), and hence total arsenic, was *ca.*50 % lower than in the absence of limestone. Possible contributing factors to this effect are:

i) Fe(III) leached from the sandstone under acidic conditions is precipitated on contact with the limestone base.

ii) The As(III) is oxidised to As(V) by Fe(III) on the surface of the limestone and by FeO(OH)(s) precipitated in the buffered solution.

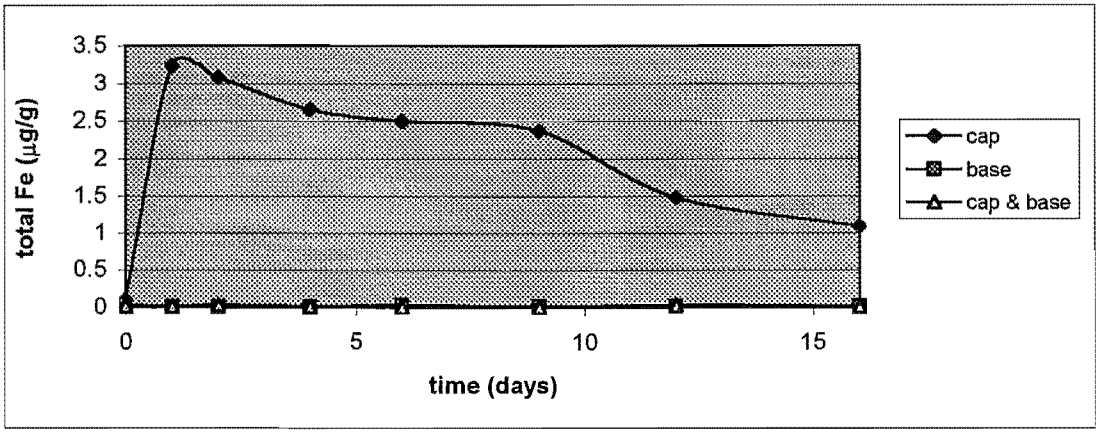
iii) As(V) is adsorbed by the precipitated FeO(OH).

iv) AsO_4^{3-} is dissolved in the acid leachate and the H^+ released attacks limestone which in-turn releases Ca^{2+} to form the precipitate $Ca_3(AsO_4)_2$ within the limestone layer at the base.

In the absence of limestone, both oxidation states were present in the leachates (Figure 7.14a. The removal of As(III) from the leachates is an important result in terms of ecological implications (e.g. toxicity). Therefore the effect of limestone on the oxidation states of arsenic merited further study (below).

c) Total Fe

Figure 8.3. Total Fe in leachates from the non-recycled Milli-Q water leaching of sandstone waste rock (50 g). Limestone layers (10 g) were placed at the cap, base, or cap and base.



The position of limestone layers had an effect on the amount of Fe leached from the column as shown in Figure 8.3. This appears to be connected to leachate pH. After 16 days with limestone as a capping layer, the amount of Fe leached was *ca.* 25 % than that leached by milli-Q water (without limestone layers), results of which are given in Figure 7.15 in Chapter 7. This suggests that the alkalinity generated by the dissolution of the limestone cap initially immobilised Fe at the top of the column but as the pH of the leachate drops further down the column Fe remains in solution. However, with the placement of limestone at the base or as both cap and base layers, the total Fe in the leachates was low (<0.030 µg/L). After dissolution in the upper (acidic) parts of the column, the oxidised Fe was subsequently precipitated as ferric hydroxide on contact with

the basic layer of limestone. This yellow brown material was observed at the base limestone layer. This precipitate may also have included arsenates.

d) Heavy metals

Table 8.1: ASV-labile metals from the non-recycled Milli-Q water leaching of sandstone waste rock (50 g) at days 0 and 16. Limestone layers (10 g) were placed at the cap, base, or cap and base.

Limestone placement	Cu (μg/g)		Pb (μg/g)		Cd (μg/g)		Zn (μg/g)	
	0 d	16 d	0 d	16d	0 d	16 d	0 d	16 d
Cap	0.0001	0.01	0.0001	0.02	0.005	0.01	0.004	0.01
Base	0.004	0.004	0.001	0.001	0.001	0.002	0.04	0.01
Cap & Base	0.005	0.0007	0.0007	0.001	0.001	0.0007	0.005	0.001

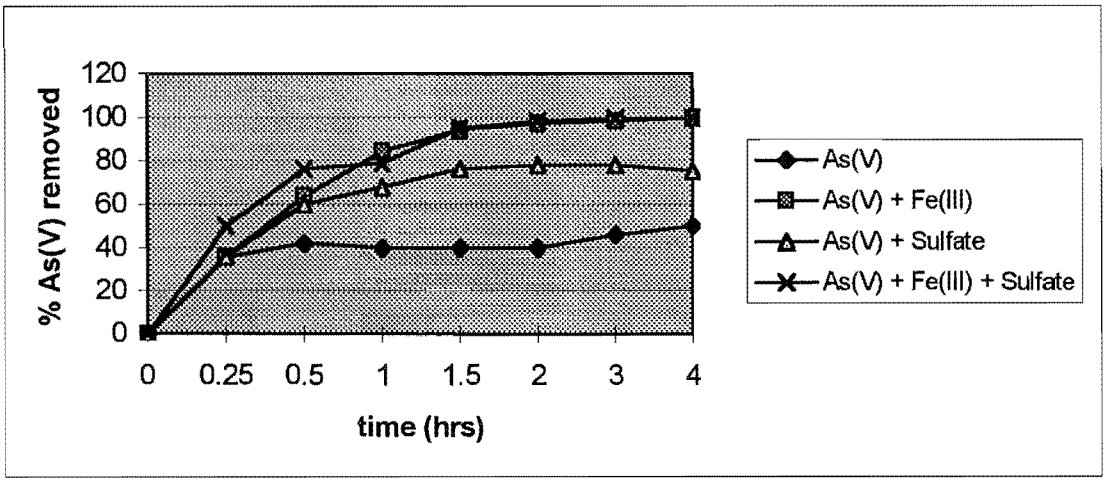
The error for the lowest value (0.0007 μg/g) is 0-10 % SD from the mean.

The data in Table 8.1 indicate that leachates from the sandstone contain measurable concentrations of ASV-labile metals. These results can be compared with those given in Table 7.4 for similar leaching of the waste rock (without limestone layer). The amount of ASV-labile metal entering the leachate from the sandstone was reduced by action of limestone layers. For example at 16 days (cap and base), there was a reduction of leached Cu concentration by a factor of 28 and Pb by a factor of 30. It can be inferred that the decrease in the concentration of heavy metals was due to adsorption to FeO(OH) precipitates formed at the limestone base.

8.4.1.2 Synthetic solutions

The removal of arsenic from synthetic solutions was examined through recycled leaching tests using the solutions described in section 8.3.2. The results and discussions for total Fe and As(V) are presented in this section.

Figure 8.4: Results for As(V) removal from 5 ppm As(V) solutions (30 mL) (pH 3.0) by limestone, in the presence of Fe(III) (20 ppm) and/or, SO_4^{2-} (200 ppm) recycled over limestone.



The results for arsenic removal shown in Figure 8.4 indicate that when solutions are recycled over the layer of limestone As(V) is depleted from solutions containing Fe more effectively than if arsenate alone is present. This is because of $Fe(OH)_3$ (or FeO(OH)) precipitation, which is enhanced by the limestone (alkaline condition) (see Figure 8.3), and consequent adsorption of arsenate, forming ferric arsenate ($FeAsO_4$) (see equation 8.1).

Figure 8.4 shows that As(V) is also removed from solution in the absence of added Fe although to a lesser extent than in its presence. On contact with limestone the leachate becomes weakly alkaline and there is a significant increase in the concentration of dissolved calcium. The alkalinity and/or calcium could in principle, be responsible for the removal or depletion of As(V) from the leachates. Thus, possible reactions are precipitation of As(V) as calcium arsenate, e.g. $Ca_3(AsO_4)_2$ or $Ca_{10}(AsO_4)_6(OH)_2$) according to equations 8.2 and 8.3.

$$H_3AsO_4 + Fe(OH)_3\,(s) \text{ ----------> } FeAsO_4.\,2H_2O\,(s) + H^+ \qquad (8.1)$$

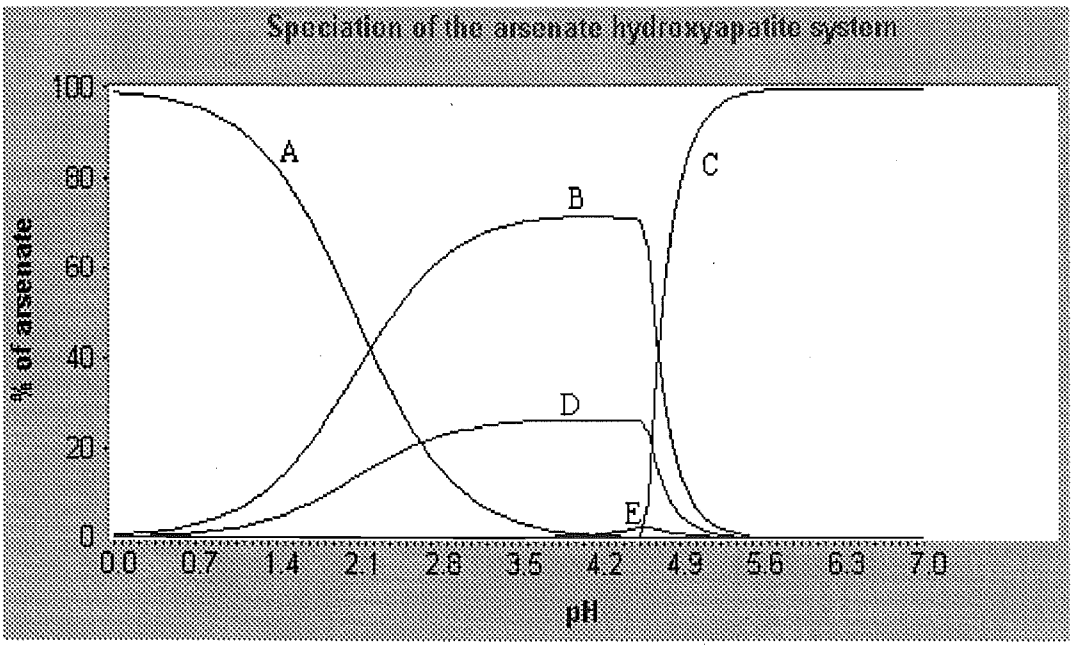
$$3Ca^{2+} + 2HAsO_4^{2-} \text{ ----------> } Ca_3(AsO_4)_2\,(s) + 2H^+ \qquad (8.2)$$

$$10Ca^{2+} + 6AsO_4^{2-} + 2OH^- \text{ ----------> } Ca_{10}(AsO_4)_6(OH)_2(s) \quad (8.3)$$

$$3Fe^{2+} + 2HAsO_4^{2-} \text{ ----------> } Fe_3(AsO_4)_2\,(s) + 2H^+ \quad (8.4)$$

Calculations with the program SPECIES (Pettit and Powell, 1999) indicated that reaction 8.2 could not be responsible for removal of As under the experimental conditions (i.e. the solubility product was not exceeded). However it was established that formation of the sparingly soluble complex $Ca_{10}(AsO_4)_6(OH)_2(s)$ could control the solubility of As(V) in the leachates exposed to high concentration of Ca^{2+} from the limestone layer. The speciation diagram for this system (Figure 8.5) was calculated based on stability constants from Mahapatra *et al.* (1987). The stability constants for these are given in Table 8.2, for 15.0 and 0.067 mmol calcium and arsenate respectively.

Figure 8.5: The species diagram for the system Ca^{2+}-H^+-AsO_4^{3+}as the function of pH.



A is H_3AsO_4, B is $H_2AsO_4^-$, C is $Ca_{10}(AsO4)_6(OH)_2(s)$, D is $CaH_2AsO_4^+$ and E is $CaHAsO_4$.

Table 8.2: The stability constants for a calcium hydroxyapatite system:

$$pCa^{2+} + qH^{+} + r(AsO_4^{3-}) = Ca_p\,Hq\,(AsO_4^{3-})_r$$

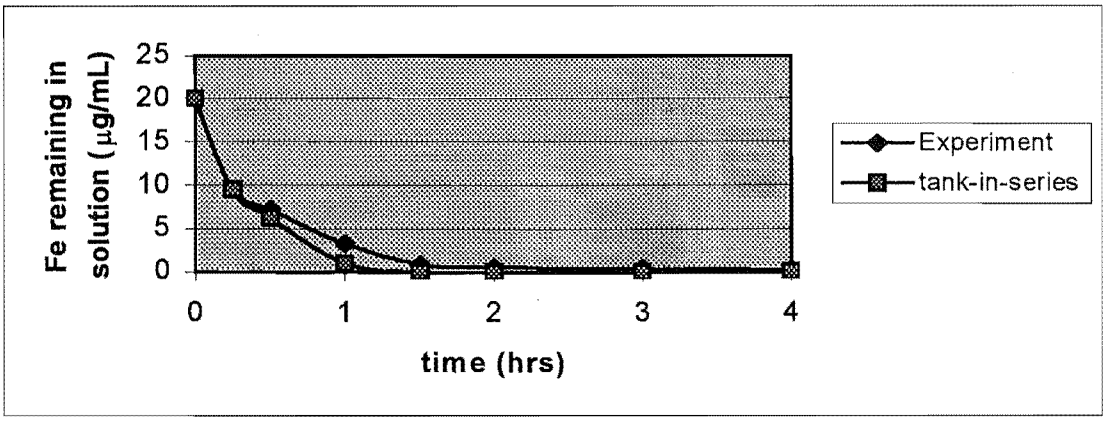
Reactants	Log $\beta_{p,q,r}$	p	q	R
Arsenate	11.51	0	1	1
	18.44	0	2	1
	20.65	0	3	1
Ca^{2+}-H^{+}- AsO_4^{3-}	4.3	1	0	1
	14.26	1	1	1
	19.83	1	1	2
Ksp ($Ca_{10}(AsO4)_6(OH)_2$	-90.4			

Another possibility is that in the absence of added Fe(III) As(V) is retained by the limestone surface via interaction with surface components, most likely lattice Fe. Dissolution of Fe(II) from the limestone surface and reaction with arsenate to form insoluble ferrous arsenate as shown in equation 8.4 was also considered, but calculations showed that the reaction would not proceed under the experimental conditions. Also any Fe(II) dissolved from the limestone would be oxidised to Fe(III), hydrolyse and precipitate as $Fe(OH)_3$ under weakly alkaline pH conditions generated by the limestone.

The role of sulfate is not clear. Sulfate can compete for arsenate adsorption sites on $Fe(OH)_3$, (Rose and Ghazi, 1997), or for active Ca and Fe sites on the limestone. However the Fe-SO_4^{2-} reaction is weak compared with Fe-AsO_4^{3-} which accounts for the removal of arsenate. The result in Figure 8.4 actually shows a small enhancement of As(V) removal in the presence of sulfate.

The removal of Fe from the solution containing 5 ppm As(V) and 20 ppm Fe recycled over a layer of limestone shown in Figure 8.6 where the data are plotted as Fe remaining in solution.

Figure 8.6: The removal of Fe from a solution (pH 3.0) of 5 ppm As(V) and 20 ppm Fe recycled over a layer of limestone.



It can be shown that the same proportion of Fe (and As(V)) is removed from the leachate each time it contacts the limestone. For a recycled solution this is established because the "decay curve" is consistent with the tank-in-series model. For this work it was equivalent to monitoring the mean Fe concentration of the accumulated leachate at specific time intervals. This is based on the concept of liquid flow through a series of ideally stirred tanks of equal size and consequent dilution of the substrate (Ruzicka, 1988). For a single tank it is quantitatively described by the equation 8.5:

$$C/C^\circ = 1/Ti\ e^{-t/Ti} \qquad (8.5)$$

where Ti is the mean residence time of a specific volume of solution (leachate) in the tank and t is the elapsed time. From this we can write expression 8.6 for the tank-in-series model.

$$C/C^\circ = \alpha\ e^{-x},\ \text{where } x = Qt/V_m \qquad (8.6)$$

Q is the total volume that has passed through the tank in time t, and V_m the total tank volume and α is a constant. For the system used the solution flow rate was 72 mL/h, V_m 30 mL and α was calculated to equal 0.56.

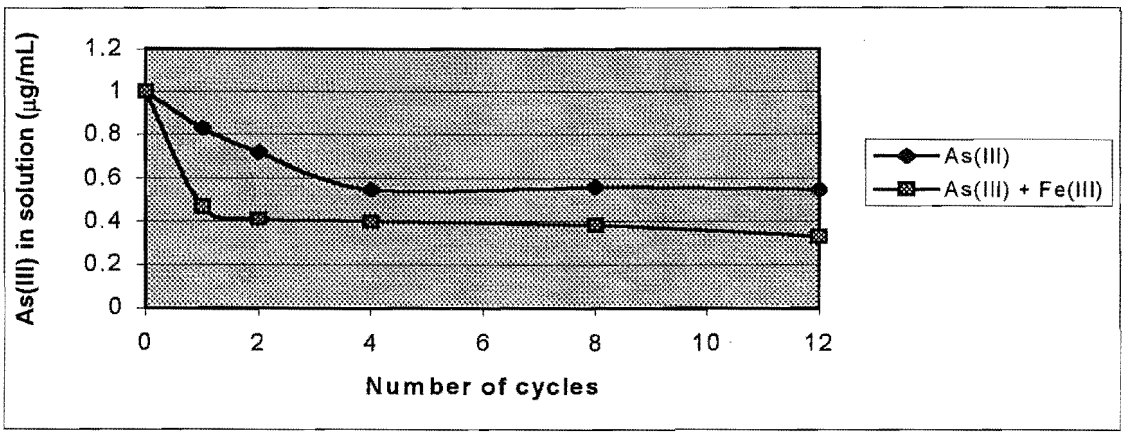
8.4.2 Removal of As(III)

Experiments were carried out to establish whether As(III) interacts with surface Fe on the limestone and is oxidised, or whether it is captured by the precipitated ferric hydroxides. The results for these experiments are shown in the following section.

8.4.2.1 As(III) interaction with limestone

Figure 8.7 shows the effect of limestone on As(III) concentration in solution in the absence and presence of Fe(III).

Figure 8.7: Results for a 30 mL solution (pH 3.0) containing 1 ppm As(III) and 20ppm Fe(III) recycled over limestone.



The role of the limestone surface in affecting the solubility of arsenic was also studied by recycling an As(III) solution over limestone in the absence of added Fe(III), measuring the As(III) remaining in solution and the As(III) and As(V) adsorbed to the limestone (after desorption with 0.1 M HCl). Table 8.3 shows the results for this experiment.

Table 8.3: The effect of the limestone surface on a recycled solution of 1 ppm As(III) measured at 1hr and 24 hrs.

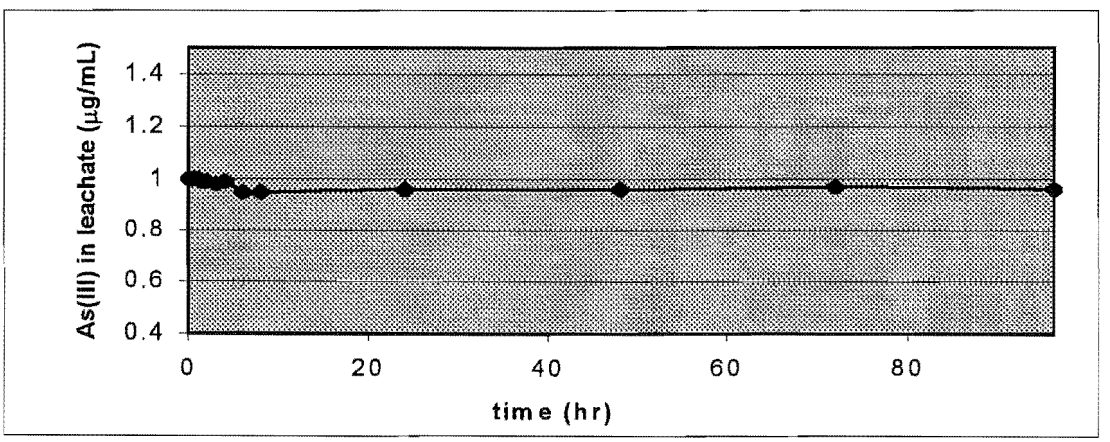
Solution treatment	As(III)*	As(III)+	As(V)#	Added As (III)
1hr recycling	830	44	100	1000
24 hr recycling	630	120	250	1000

* As(III) remaining in solution recycled over limestone; + As(III) desorbed from limestone surface; # As(V) leached from limestone surface. Concentrations shown are expressed as ppb. Errors are within 0-10% RSD. Errors are within 0-10% RSD.

8.4.2.2 As(III) in presence of limestone equilibrated water

The tendency for As(III) to be oxidised in solution under weakly alkaline conditions was monitored for a solution of As(III) in limestone equilibrated water (Figure 8.8).

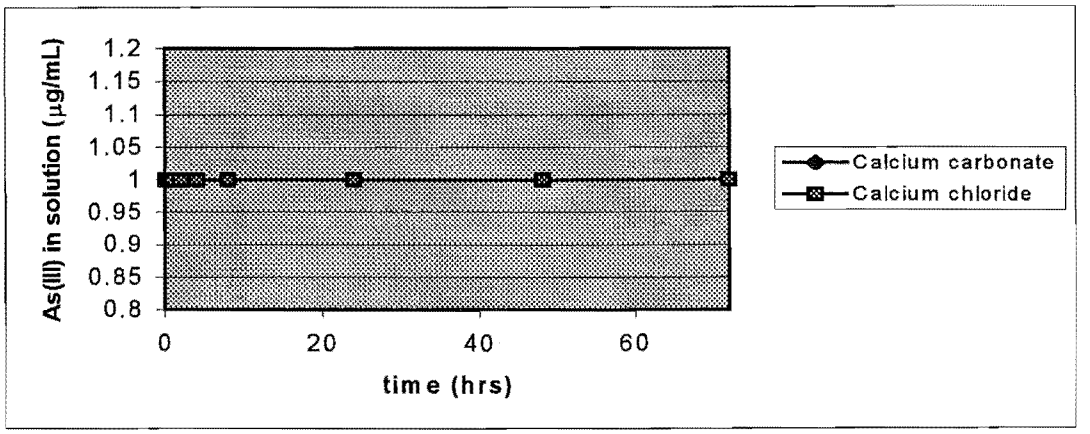
Figure 8.8: As(III) (1 ppm) in limestone equilibrated water (pH 8.4).



8.4.2.3 The effect of calcium chloride and carbonate on As(III)

The effect of Ca^{2+} in calcium chloride and carbonate solutions on the solubility of As(III) was studied (Figure 8.9).

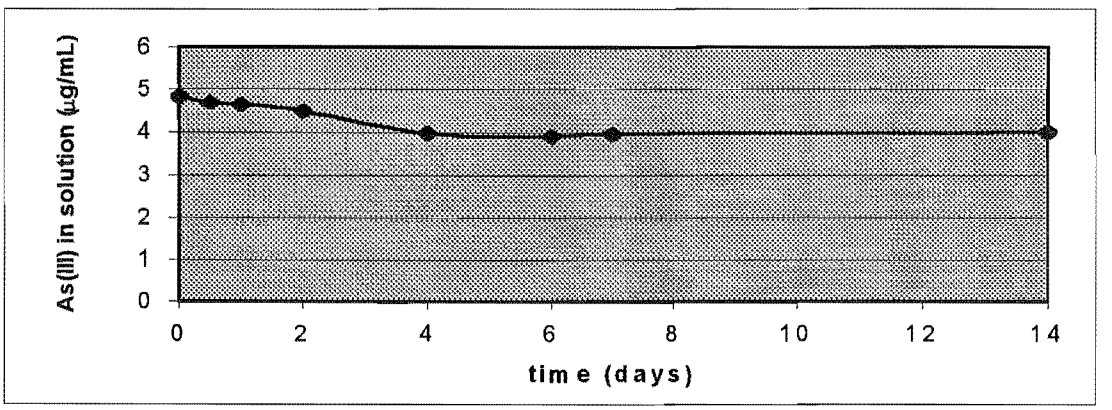
Figure 8.9: 1 ppm As(III) in calcium chloride and carbonate solutions. The calcium concentration was 800 ppm.



8.4.2.4 Effect of Fe(III) on As(III) in solution at pH 3.0

It was known that As(III) is oxidised in contact with $Fe(OH)_3$ (s). However experiments were also conducted to establish whether oxidation could be effected by Fe(III) in homogeneous solution. The results are given in Figure 8.10 which shows that after 4 days the As(III) concentration has dropped to 80 % of the initial concentration.

Figure 8.10. The loss of As(III) by oxidation in a solution containing 5 ppm As(III) and 40 ppm Fe(III) at pH 3.0.



From the results in sections 8.4.2.1-4 it can be seen that As(III) is removed from solutions which are recycled over layers of limestone. Table 8.3 indicates that oxidation of As(III) to As(V) occurs and both As(III) and As(V) are retained on the limestone surface. Oxidation probably occurs at Fe(III) centres on the limestone surface and retention also

occurs at the Fe(III) surface sites. Results in Figure 8.7 indicate a 35 % greater removal by the limestone in the presence of 20 ppm Fe(III) than in its absence. This depletion of As(III) could be due to oxidation of As(III) to As(V) on, then adsorption by, ferrihydrite (ferric hydroxide).

Supporting this interpretations, oxidation of As(III) to As(V) did not occur in limestone equilibrated water (Figure 8.8), calcium carbonate, or calcium chloride solutions (Figure 8.9). In the presence of limestone, arsenite oxidation is therefore a surface process. The pH of the calcium solutions (~8.3) was less than the minimum (10.5) required for complexation of arsenite (0.3 μg/mL) (Nishimura and Robins, 1998).

Figure 8.10 indicates that in the absence of limestone at pH 3.0, ~20 % of As(III) was oxidised to As(V) in the presence of Fe(III) in solution. Thermodynamic calculations (equations 8.7 and 8.8) show a favourable ΔG°_{f} for arsenite oxidation by both solution and solid phase Fe(III) .

At pH 3.0 Fe(III) will be present as $Fe(OH)_2^+$

$$H_2AsO_3^- + 2H^+ + 2Fe(OH)_2^+ \text{ ----------> } H_2AsO_4^- + 2Fe^{2+} + 3H_2O \qquad (8.7)$$

(ΔG°_{f} = -154.5 kJ/mole)

FeOOH (*amorphous*) in surface of limestone as the oxidant

$$H_2AsO_3^- + 4H^+ + 2FeOOH \text{ ----------> } H_2AsO_4^- + 2Fe^{2+} + 3H_2O \qquad (8.8)$$

(ΔG°_{f} = -108.3 kJ/mole)

For both reactions although thermodynamics are favourable, kinetic factors may significantly limit the rate of reaction.

8.4.3 Role of the limestone surface

It was observed in 8.4.1.2 that there was some uptake of As(V) by the limestone surface in the absence of FeO(OH) precipitated from solution Fe. Therefore it was appropriate to establish whether the uptake was by Ca or Fe at surface sites on the limestone. Experiments were conducted to determine the active sites on the limestone surface. The results and the discussion are presented in this section.

8.4.3.1 Solid state properties of limestone

Two limestones were studied, one (Reefton) with low Fe content, the other (Mt. Somers) with high Fe content and a pale ochre appearance. The Fe contents of the bulk samples were quantified by XRF analysis. Results are given in Tables 8.4 (excluding trace components present at < 400 μg/g).

a) XRF data on limestone

Table 8.4: Major elements by XRF for Mt. Somers and Reefton limestones.

Compound	Mt Somers (%)	Reefton (%)
Fe_2O_3	0.96	0.27
MnO	0.02	<0.01
MgO	0.42	0.66
CaO	52.83	52.8

X-ray fluorescence (XRF) measurements confirmed that apart from calcium and magnesium, Fe was the major cationic component in limestone.

b) Mossbauer spectroscopy

Mossbauer spectroscopy measurements were made on the high Fe content (Mt. Somers) limestone to establish the oxidation state of Fe in the limestone. Results are shown in Table 8.5.

Table 8.5. Mossbauer data for the Mt Somers limestone.

Limestone	Quadrupole splitting	Chemical Shift
Mt Somers	0.532 ± 0.04 mm/sec	0.377 ± 0.025 mm/sec

For the limestone sample, Mossbauer spectroscopy exhibited a chemical shift of 0.377 ± 0.025 mm/sec and a quadrupole splitting of 0.532 ± 0.04 mm/sec. This velocity can be assigned to Fe(III) as γ FeOOH (lepidocrocite) (Greenwood and Gibb, 1971) in the bulk limestone sample. There are no available Mossbauer data for $Fe_2(CO_3)_3$ hence the involvement of this species cannot be discounted. Importantly the result indicates that Fe(III) in the limestone could be the surface reactive component responsible for the oxidation of As(III) and the retention both arsenic species.

8.4.3.2 Establishing the active sites

Experiments were conducted with the Mt. Somers limestone to establish whether Fe or Ca was the active site in the limestone surface that was interacting with As(III) and As(V). Ascorbic acid was used to reduce Fe(III) on the limestone surface to Fe(II). If Fe(III) is the active site then reduction would inhibit uptake of As(V). In the second experiment 1.10-phenathroline was used to mask Fe(II) formed. The results are shown Table 8.6 and Figure 8.11.

a) Fe sites

To establish whether Fe(III) was the active site the limestone was pretreated with solutions containing:

i) 5 % ascorbic acid and 0.1 M acetate buffer (pH 5.0).

ii) 5 % ascorbic acid, 10^{-4} M phenanthroline and 0.1 M acetate buffer (pH 5.0).

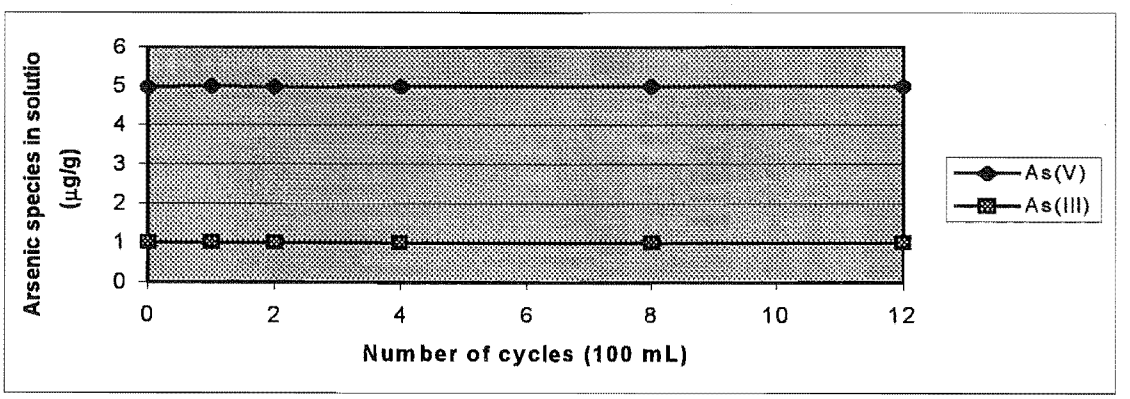
Table 8.6: Retention of 5 ppm As(V) solution by limestone (30 g) after pre-treatment of the limestone with a solution (250 mL) containing 5 % ascorbic acid and 0.1 M acetate buffer (pH 5.0) for 1 hr. The volume of the 5 ppm As(V) solution (pH 3.0) was 100 mL and was recycled over the pre-treated limestone for two cycles.

Solution	As(V) (μg/mL)
As(V) in initial solution	5.00
As(V) remaining in solution	4.70
As(V) removed from solution	0.30
As(V) removed from solution*	1.8

* The concentration of As(V) retained from a reference solution (5 ppm As(V)) when no ascorbic acid used. Errors are within 0-10% RSD.

The results in Table 8.6 indicate that only 6% of As(V) was retained by the treated limestone surface. In contrast 30 % of As(V) formed from oxidation of As(III) was retained from a 1 ppm solution after two cycles over untreated limestone (Figure 8.7). This indicates a reduced number of sites for the uptake of As(V) after ascorbic acid treatment of the limestone. This residual retention may have been by Fe(II) on the limestone surface resulting from the ascorbic acid reduction. Therefore, the next experiment involved inclusion of phenanthroline to mask any Fe(II) formed.

Figure 8.11: Results for 5 ppm As(V) and 1 ppm As(III) passed over limestone pre-treated with 5 % ascorbic acid and 10^{-4} M phenanthroline at pH 5.0 (acetate buffer). The limestone was pre-treated by recycling with a 250 mL of acetate/ascorbic/ phenanthroline for 1 hr. The volume of the arsenic solutions (pH 3.0) was 100 mL.

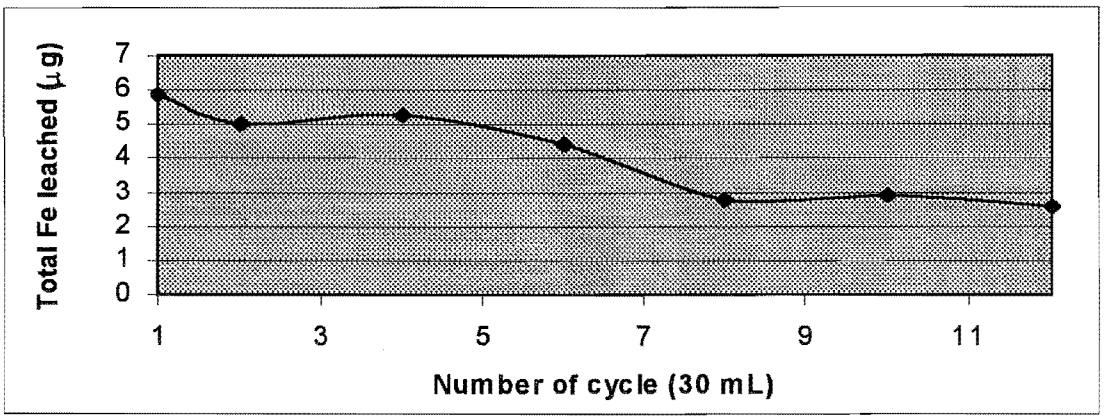


The results in Figure 8.11 show that there was neither As(III) oxidation nor the retention of arsenic species following masking of Fe(III) on the limestone surface with ascorbic acid and phenanthroline. These results indicate that in limestone Fe(III) is the main surface reactive component responsible for the oxidation of As(III) and for the retention of both arsenic species, through the formation of iron (III) arsenate and arsenite complexes.

b) Effect of AMD on reactive sites on limestone

An experiment was conducted to establish whether new Fe (reactive) sites on the limestone surface are generated as a result of the surface being exposed to AMD at pH 3.0. The pH of 3.0 simulates the pH of water equilibrated with the sandstone acidic waste rock. The results are shown in Figure 8.12.

Figure 8.12: The effect of repeated exposure of limestone to 0.001 M sulfuric acid, simulating the effect of AMD on limestone surfaces.



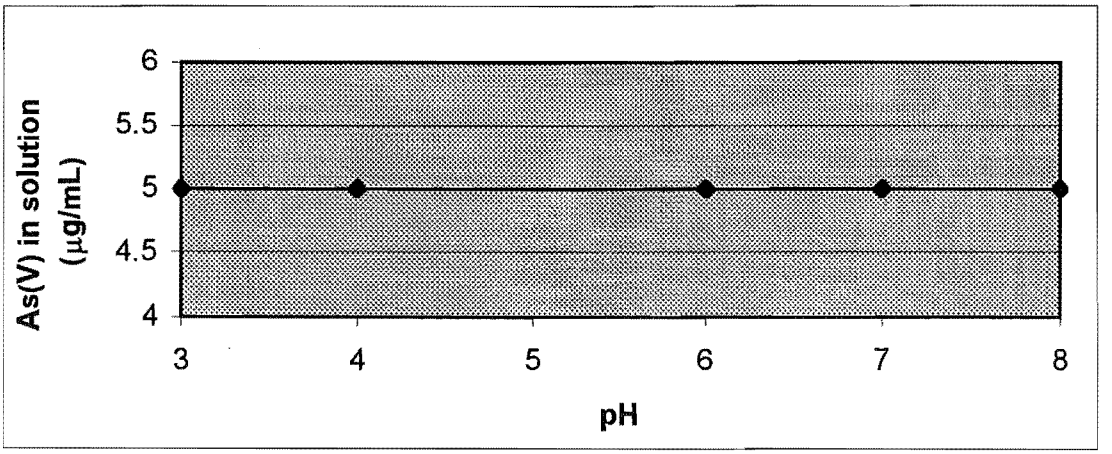
The results in Figure 8.12 show that the concentration of Fe in the leachate decreased from 6 µg to 2.5 µg when exposed to dilute sulfuric, pH 3.0. This implies that Fe is leached from the surface more rapidly than limestone is dissolved to expose more surface Fe sites so that the Fe on the surface of the limestone was gradually depleted. There is may also the formation of a surface coating of $Fe(OH)_3$ reducing the dissolution of Fe. The amount of Fe dissolved would depend also on contact time of the AMD with the limestone surface. Dissolved Fe(III) combined with surface Fe(III) can provide the immobilising medium for As(V) and also facilitate the oxidation of As(III). However,

dissolution of limestone may not be sufficiently rapid to expose an adequate amount of Fe(III).

c) Calcium sites

Investigation into the possible formation of solid calcium arsenate was made by reacting As(V) with calcium carbonate solution, pH 3-8. This experiment aimed to establish whether calcium from the limestone surface could contribute to the immobilisation of As(V) by precipitation of a solid phase. The calcium concentration used (1000 ppm) corresponds to a saturated solution of $CaCO_3$ released from limestone at pH 8.0. The results are shown in Figure 8.13, expressed as the concentration of As(V) after membrane filtration of the solution.

Figure 8.13: Reaction of 5 ppm As(V) with calcium carbonate at pH 3-8. The calcium concentration was 1000 ppm and the volume of these solutions was 100 mL.

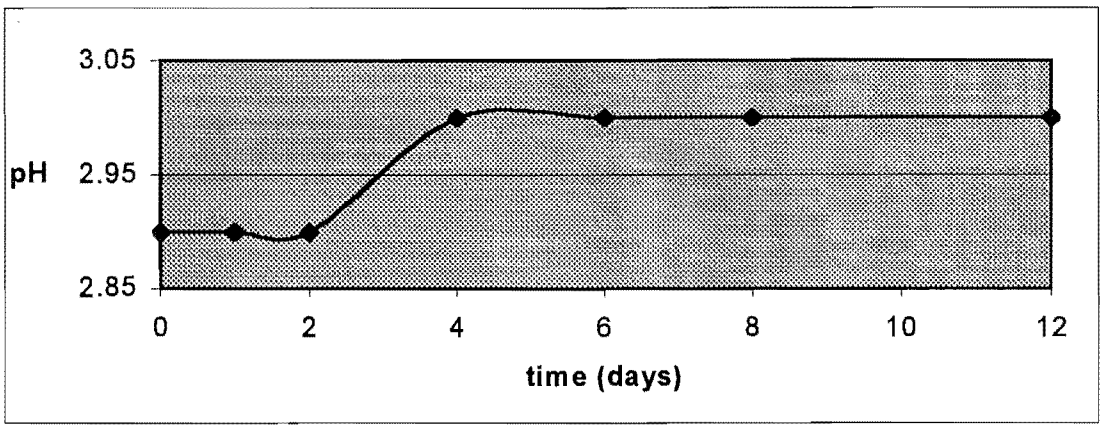


Since there was no decrease in the As(V) concentration this implies that insoluble calcium arsenates were not formed. The maximum pH of the experimental solutions studied, pH 8.0 (simulating pH of limestone equilibrated water) was lower than the minimum pH 12.1 required for the formation of the basic calcium arsenate ($Ca_2AsO_4OH.2H_2O$) (Nishimura and Robins, 1998).

8.4.4 Acid neutralising capacity of waste rocks

The acid neutralising potential of GB 13 was investigated briefly. This was to establish whether GB 13 was able to weather sufficiently rapidly to neutralise the acidity from leachates of the sandstone. If GB 13 neutralised this acidity, it could be used in place of limestone. To achieve this 30 mL of Milli-Q water was passed (non-recycled) over 30 g GB 13 placed over a layer (1 g) of sandstone. Results are given in Figure 8.14.

Figure 8.14: The acid-neutralising effect of GB 13 (30 g) on acid-producing sandstone (1 g).



Results in Figure 8.14 show that a capping layer of basic waste rock GB 13 did not provide sufficient alkalinity to counter the acidic leachates produced from the sandstone. The performance of GB 13 as a base layer was not investigated.

8.5 CONCLUSION

The ability of the limestone to consume acid and to immobilise As has obvious implications for control of the contaminant arsenic in a waste rock stack. These experiments showed that where acidic rock drainage occurs, contact with limestone at the base of the rock stack raises the pH as a result of neutralisation reactions. Subsequently there is a precipitation of Fe(III) and retention of As(V) on the $Fe(OH)_3$. The more toxic As(III) is also retained and oxidised on contact with limestone. As(III) is also oxidised by $Fe^{3+}(aq)$ and $Fe(OH)_3$.

It has been established that the Fe(III) impurities in the limestone are responsible for the uptake of both As(V) and As(III). The mechanism of As(III) retention by Fe(III) involves As(III) capture by Fe(III) sites in the solid phase, oxidation to As(V), followed by formation of ferric arsenate.

The pH of limestone equilibrated water (pH 8.3) is below the pH required for the precipitation of calcium arsenates, hence these compounds are not formed in limestone-treated leachates.

As a capping layer the basic waste rock GB 13 does not dissolve to produce alkalinity sufficiently rapidly to counter acidic leachates from the sandstone. It would be worthwhile to investigate its performance as a base layer. The suggested control measure for arsenic generation in the waste rock stack would be to pack the base of the stack with limestone or sufficiently reactive carbonate containing waste rocks from within the ore body.

CHAPTER 9

CONCLUSION

Study into the problem of acid mine drainage and associated arsenic speciation has been the major thrust in this work. This has involved arsenic containing waste rocks GB 13 and sandstone taken from a proposed mine site at Reefton, New Zealand. Laboratory leaching studies were carried out on the waste rocks and the inorganic arsenic species As(V) and As(III) quantified in the leachates. The control of acidity and arsenic solubility in the leachates by use of limestone layers was also investigated.

Leachates from the mine site would enter Devils Creek. The fresh water and sediments in the Devils Creek catchment (in the vicinity of the proposed mine site) were analysed for arsenic. To simulate the interaction of sediments with the water column, synthetic ferrihydrite was investigated for its interaction with arsenate. Adsorption studies were carried out in the presence and absence of HA, FA, HA-Fe(III), FA-Fe(III), sulfate and calcium.

METHOD DEVELOPMENT

A method using XAD-4 and Chelex-Fe(III) resins was developed to fractionate arsenic in fresh water samples. It is simple and convenient for on site As fractionation and is the preferred method when there is a long delay time between field work and analysis in the laboratory. In this two-step process the XAD-4 resin isolates and pre-concentrates natural organic matter (NOM) and therefore the arsenic fraction associated through iron bound to the NOM. In the second step Fe(III) modified Chelex 100 resin is used to selectively preconcentrate As(V) from water samples. Thus the combined method achieves discrimination between free and bound fractions of As(V) and the separation As(V) from As(III).

ARSENIC IN THE CATCHMENT

The water in Devils Creek Catchment contains high concentrations of arsenic. Most of the arsenic is soluble. As(V) is the predominant species of which a minor fraction (13-28%) is bound to NOM. The low As(III) concentration is most likely a result of oxidation to As(V), facilitated by the high pH of the freshwater (*ca.* 7.1) and through interaction with suspended and bottom sediments that contain hydrous oxides of manganese and iron. The total arsenic concentration of ~145 μg/L (4 km downstream) is significantly above the WHO recommended drinking water level of 10 μg/L.

When AMD is released into a fresh water arsenate can be removed semi-quantitatively and rapidly through interaction with ferrihydrite. The arsenate adsorption is inhibited by sulfate, FA, and HA. Complexes of HA-Fe(III) and FA-Fe(III) bind arsenate as 1:1 adducts through the Fe(III).

Arsenic was associated with Fe and Al rich phases in the Devils Creek sediments. The high concentration of arsenic in the water and sediments could arise from the natural geological materials and from leaching of old mine workings within the Devils Creek catchment. The high accumulated arsenic load in the sediments (up to 5 km downstream) prevents further uptake of arsenic from the water column because potential binding sites in the sediments have been saturated. Therefore any further arsenic added to the water column (e.g. from mining activities) would be transported downstream without interacting with sediments. The impact of lowering the pH in the catchment to below pH 4.5 because of AMD is likely to be desorption of arsenic from the sediments into the water column, resulting in increased soluble arsenic.

It has been suggested that pH alone is an adequate measure of AMD impacts on a catchment. However this work shows that the pH is not a good indicator to monitor occurrence of arsenic in waste rock leachates and fresh waters. This work has established that significant amounts of arsenic are present in Devils Creek water even though the pH is 7.1.

WASTE ROCK LEACHING (OXIC AND ANOXIC)

The sandstone waste rock contains both pyrite and arsenopyrite and generates an acidic pH of 2.8. Therefore it has the greatest potential to produce acid mine drainage (AMD). The immediate acidity on contact with water could be a result of accumulated surface oxidation products e.g. ferric salts and jarosite ($K[Fe(SO_4)_2Fe(OH)_3]$). The Fe(III)/Fe(II), total Fe/sulfate and total As/sulfate ratios produced in leachates are increased in the presence of oxygen relative to anoxic conditions. Furthermore, oxygen gives rise to Fe(III) dominance under an oxic environment, whereas Fe(II) dominates under anoxic conditions. Considering the time dependent concentrations of Fe, SO_4^{2-} and As produced in solution, it is apparent that the rate of increase slows significantly with time. This may relate to a decrease in the rate of dissolution of FeAsS and FeS_2 from the rock. It is proposed that a passivating layer develops and coats the rock surface, slowing down dissolution. This layer is most likely $Fe(OH)_3$. For Fe and As, there may be a combination of reduced rate of FeAsS and FeS_2 dissolution and an increased precipitation of Fe or adsorption of and As.

Leachates of the GB 13 waste rock give rise to a weakly basic pH of 7.2. The pH of leachates both waste rocks controls the pH of the leaching solution used (rain, humic or Milli-Q water). There was no significant effect on the rate of leaching for each waste rock when different types of leachants were used. The dominant arsenic species in leachates of both rock samples is As(V). This is consistent with measured E and pH values. The concentrations of arsenic, soluble Fe and heavy metals leached from the sandstone were greater than those leached from GB 13. The Fe levels significantly contribute to the measured value of E; this is inferred from the agreement between measured E (therefor E_h) and the E_h calculated using the Fe(II)/Fe(III) redox couple.

FIELD IMPLICATIONS

This study indicated that the release of As, Fe, SO_4^{2-} and acidity by percolation of rainfall through the upper layer (oxic) in a waste rock stack decrease with time. As the leachate percolates down to the lower regions of the stack it becomes saturated with

AMD components such as Fe and As(V). There is some coating of rock surfaces with $Fe(OH)_3$, thus slowing the leaching process. This coating will adsorb some of the arsenic from the leachate.

It can be postulated that the prolonged coating of surfaces by $Fe(OH)_3$ within the waste rock stack can lead to As(III) and As(V) capture and the oxidation of As(III) to As(V). Thus the immobilisation of the arsenic species could lead to reduced arsenic levels at the leachate outlet from a waste rock stack.

CONTROL OF ARSENIC SOLUBILITY

The development of control strategies depends on the reliable prediction of AMD generation of the waste rocks. This work has established that AMD is produced by acidic rocks such as sandstone. It has also been established that limestone layers can be used to control leachate acidity and the mobility of arsenic. Where acidic rock drainage occurs, contact with limestone at the base of the rock stack raises the pH as a result of neutralisation reactions. The mechanism for arsenic removal by the limestone involves:

- Precipitation of soluble Fe(III) and retention of As(V) on the $Fe(OH)_3$. As(III) is also oxidised by $Fe^{3+}(aq)$ and $Fe(OH)_3$.
- Fe(III) impurities in the limestone capture both As(V) and As(III). The mechanism of As(III) retention by Fe(III) involves As(III) capture at Fe(III) sites in the solid phase, oxidation to As(V), followed by formation of a ferric arsenate. Insoluble calcium arsenates are probably not formed in limestone-treated leachates.

The ability of the limestone to consume acid and to immobilise As(III) and As(V) through (i) precipitation of $Fe(OH)_3$ and (ii) the limestone's Fe(III) centres, has obvious implications for control of the contaminant arsenic leached from a waste rock stack.

An important criterion to be identified before designing control measures is the length of time the control measure must remain effective. This has not been investigated in this work on limestone. However, it is been reported that limestone has limitations in control of AMD due to formation of a passive $Fe(OH)_3$ coating at its surface. Therefore it may not be effective for long-term AMD control. But some other long-term control method may not be as cost effective as limestone, which is still the cheapest material for AMD control. The suggested control measure for arsenic generation in the waste rock stack would be to pack the base of the stack with limestone or sufficiently reactive carbonate containing waste rocks from within the ore body.

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